ESTCP
Cost and Performance Report

(ER-0130)

Applied Innovative Technologies for Characterization of Nitrocellulose and Nitroglycerin Contaminated Buildings and Soils

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ACRONYMS AND ABBREVIATIONS

ACM	asbestos-containing material
Acetone	CH3COCH3
BAAAP	Badger Army Ammunition Plant
Ca	calcium
Cd	cadmium
CH_3COCH_3	acetone
CRREL	Cold Regions Research and Engineering Laboratory
DNT	dinitrotoluene
DoD	Department of Defense
EPA	Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
GC	gas chromatography
GC/TID	gas chromatography/thermionic ionization detection
HPLC	high-performance liquid chromatography
kVA	kilovolt-ampere
MCAWW	Methods for the Chemical Analysis of Wastewater
MSDS	Material Safety and Data Sheets
NC	nitrocellulose
ND	not determined, no detection
NG	nitroglycerine
ng	nanogram(s)
nm	nanometer(s)
NMT	not more than
OSHA	Occupational Health and Safety Administration
PETN	pentaery thertol tetranitrate
PPE	personal protective equipment
QC	quality control
RDX	Royal Demolition Xplosive
RP	rocket paste
RPD	relative percent difference
Sandia	Sandia National Laboratories

Shaw	Shaw Environmental & Infrastructure, Inc.
SRI	SRI Instruments, Inc.
ss	stainless steel
STL	Severn Trent Laboratories, Inc.
SUXOSO	Shaw UXO Safety Officer
TDL	Technology Development Laboratory
TID	thermionic ionization detection
TNT	trinitrotoluene
USACE	U.S. Corps of Engineers
UV	ultraviolet
UXO	unexploded ordnance
w/v	weight/solvent volume
WDNR	Wisconsin Department of Natural Resources
Zn	zinc

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Technical material contained in this report has been approved for public release.

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1.0 EXECUTIVE SUMMARY

1.1 BACKGROUND INFORMATION

Badger Army Ammunition Plant (BAAAP), in Sauk County, Wisconsin, is one of many inactive Army ammunition plants currently under the control of the Department of Defense (DoD) with transitioning missions in place. These plants are in varying stages of transfer out of DoD control. In order to transfer these properties, DoD must characterize and decontaminate the properties to a level protective of human health and the environment. To accomplish this task, many buildings used in the production, loading, handling, and storage of explosives will have to be demolished or characterized and decontaminated. BAAAP alone has more than 1,400 buildings on the installation that have to be addressed. The contaminants of concern associated with the buildings at BAAAP include nitrocellulose (NC), nitroglycerine (NG), dinitrotoluene (DNT), and common environmental compounds such as asbestos-containing material (ACM), solvents, and metals.

A previous Environmental Security Technology Certification Program (ESTCP) demonstration was performed between April 28, 2002, and May 13, 2002, to demonstrate candidate field test methods for NC and NG. The methods evaluated were Raman spectroscopy, EXPRAY^{TM} colorimetric indicator, and the Cold Regions Research and Engineering Laboratory (CRREL) Royal Demolition Xplosive (RDX) colorimetric field screening method. The methods were used to test for the presence and/or concentration of NC or NG in soil samples and concrete slabs. Attempts were made to compare the results from these field measurements to laboratory analyses of NC and NG in the same materials to evaluate the reliability of the field screening and analytical methods for identifying and quantifying NC and NG in buildings and soils. The results of the previous demonstration and lessons learned were presented in the Phase I Final Report, Rocket Paste Production Building Investigation, Badger Army Ammunition Plant, dated June 24, 2003, and published by Stone & Webster, Inc. (Stone & Webster, 2003). Due to a number of factors, including the lack of energetic compounds in the buildings used for the demonstration, attempts at validation of the field methods for detection of these materials were inconclusive.

This ESTCP demonstration targeted areas with higher suspected explosives contamination to obtain samples containing measurable amounts for testing. Shaw Environmental & Infrastructure, Inc. (Shaw) as the prime contractor to the U.S. Army Corps of Engineers (USACE) Omaha District performed bench-scale tests reported in the Bench-Scale Study Report (Appendix C) and the field demonstration testing reported in the Field Demonstration Report (Appendix D).

1.2 STUDY OBJECTIVES

The objectives for this ESTCP demonstration were to evaluate and document the performance of three candidate experimental field analytical methods for detecting and quantifying NC and NG associated with structural concrete pads, underlying soils, and structural building materials such as framing timbers. The technologies evaluated in the field demonstration were DROPEX^{Plus}/EXPRAY^{TM} colorimetric indicators, gas chromatography/thermionic ionization detection (GC/TID), and the CRREL RDX colorimetric field screening method.

1.3 REGULATORY ISSUES

There are no regulatory drivers per se governing this project, nor are there state or federal environmental standards for NC and NG cleanup. There is a site-specific Wisconsin Department of Natural Resources (WDNR) cleanup criterion for NG in the area soils of 3.6 mg/kg (Environmental Protection Agency [EPA] & WDNR, 1988). There is also no DoD standard for NC and NG residual contamination; however, safety concerns related to the explosive nature of these materials provide the driver for this investigation.

1.4 DEMONSTRATION RESULTS

DROPEX^{Plus} and EXPRAY^{TM} tests were found to be useful tools for screening the presence of significant concentrations of NC and or NG in the field or on sample extracts. In combination with other field methods, they are beneficial screening tools for identifying areas that contain explosive contamination in buildings above specified limits. Detectable levels are matrix-dependent, with low confidence in results at or near the detection limit.

The CRREL RDX method of analysis gave a relatively low response for NC compared to NG, and the response was easily impacted by matrix interferences. Modifications to the CRREL RDX procedure greatly increased the method response for NC and retained the response for NG. The increase in response made the modified method more robust for NC analysis and allowed analysis of NC on the three sample matrices. It is Shaw's opinion that the CRREL RDX method is not appropriate for analysis of NC or mixtures of NG and NC, especially in the matrix samples used in this study, and that the modified CRREL method developed in this study is more suitable. Neither CRREL method is specific to NG or NC and both provide a response to the total of NG and NC.

Tests conducted with NC on concrete using the CRREL methodology showed that recovery of NC from the matrix was a function of both time and the manner in which NC was deposited on the matrix due to decomposition of NC by the concrete matrix. The degradation of NC was the same effect noted in the bench test portion of testing for NG. The instability of NC/NG compounds on concrete matrix makes analysis difficult not only because of the potential impact on samples during handling and preparation, but also because of the effect on matrix standards.

Compound detection performance and concentration metrics for NC/NG using the CRREL methods compared to laboratory reference method results were not met for the three matrices. This was due to a combination of factors, including insufficient positive result data for comparison on the concrete matrix; nonhomogeneity of the soil matrix due to pieces of propellant material in the samples; and in general what was felt to be highly biased and false positive results from the reference method for NC analysis on all matrices.

GC/TID analysis of NG on soil, wood, and concrete samples was a sensitive and reliable method providing results consistent with the laboratory reference Method 8330, but the comparison of concentration results did not meet performance metrics in the field demonstration. This was attributed to insufficient positive result data on the concrete and soil matrices and matrix interference with the wood sample analyses. Both methods may be subject to matrix interference effects, and quality control (QC) samples should be included to help assess data quality. The

bench-scale study demonstrated good GC/TID results agreement with NG spike concentrations on clean background matrix samples.

1.5 STAKEHOLDER/END-USER ISSUES

By verifying these technologies, stakeholders will have additional tools that will aid in the decision-making process for transfer of property at BAAAP. The demonstration of successful field analytical methods will help streamline the property disposal process.

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2.0 TECHNOLOGY DESCRIPTION

Three distinct technologies for identifying and quantifying NC and NG in the field were evaluated by Shaw against reference laboratory method analysis. The technologies were the following:

- DROPEX^{Plus} and EXPRAY^{TM} colorimetric indicators for NC and NG
- CRREL colorimetric field screening method for total NC and NG
- GC/TID method for NG.

Each of these technologies is addressed in the following sections.

2.1 DROPEX^{PLUS} /EXPRAY^{TM}

2.1.1 Technology Development and Application

The DROPEX^{Plus} and EXPRAY^{TM} systems are commercially available test kits that consist of a set of reagents that are used in a fixed sequence on an adsorptive pad to identify a variety of explosive compounds, including NC and NG. The test reagents are the same for both DROPEX^{Plus} and EXPRAY^{TM} but the reagents are in spray form for EXPRAY^{TM} and in dropper form for DROPEX^{Plus}. Explosive compound identification is performed colorimetrically within minutes by visual inspection.

The methods provide detect/nondetect results but the positive color intensity is indicative of the degree of presence of the explosive compound(s). Performance evaluations conducted with EXPRAY^{TM} by Sandia National Laboratories (Sandia, 1995, 2001) show a detection level for trinitrotoluene (TNT) at +200 nanograms (ng) total sample, although the manufacturer claims a detection level less than this.

The methods have been used for several years for screening persons, baggage, and other items at transportation facilities. It has also been used in forensic applications to identify the presence of explosives. A modification of this method has been developed for testing for the presence of explosives in soil.

2.1.2 Process Descriptions

DROPEX^{Plus} and EXPRAY^{TM} tests for explosives are performed directly on surface wipes or on extracts of sample matrices that have been deposited onto filter paper. In these tests both wipes and sample extracts were used with the test kits. For comparison of sample results to reference methods, sample matrices were extracted with acetone (CH_3COCH_3), and the acetone extracts were spotted onto filter paper for testing.

For the EXPRAY^{TM} kit the test reagents are in spray form. The spray bottle labeled EXPRAY^{TM} No. 1 was applied briefly at a distance of about 15 cm to the extract spotted area on the filter paper. The same area was then sprayed with the EXPRAY^{TM} No. 2 bottle until slightly damp. In cases where NC or NG was detected, color change to pink or red was completed in seconds (see Figure 1).

The DROPEX^{Plus} kit was tested exactly like the EXPRAY^{TM} using the same extracts. A couple of drops of DROPEX^{Plus} Reagent No. 1 were spotted on the extract aliquot on the filter paper. Approximately 15 seconds later, a couple of drops of Reagent No. 2 were added. A similar pink or red color as for the EXPRAY^{TM} was a positive indication for the presence of NC or NG explosive compounds (see Figure 1).

Figure 1. Comparison of EXPRAY^{TM} and DROPEX^{Plus} on BAAAP Wood Extracts.

2.1.3 Previous Testing of the Technology

Testing of the EXPRAY^{TM} technology was performed in a previous ESTCP demonstration performed between April 28, 2002, and May 13, 2002. The results were presented in the Phase I Final Report, Rocket Paste Production Building Investigation, Badger Army Ammunition Plant, dated June 24, 2003 (Stone & Webster, 2003). Due to a number of factors, including the lack of energetic compounds in the buildings used for the demonstration, attempts at validation of the field methods for detection of these materials were inconclusive.

Prior to the field demonstration, a bench-scale study of the experimental technologies was conducted by Shaw, and results were described in a Bench-Scale Study Report (Appendix C). The technologies evaluated at the bench-scale level included Raman spectroscopy, EXPRAY^{TM} colorimetric indicator, GC/TID, and the CRREL RDX colorimetric field screening method. Uncontaminated soil and building materials (concrete, wood, and wallboard) from the BAAAP site were spiked with known amounts of NG, NC, and NG/NC combined at specified levels. Splits of these samples were submitted to Severn Trent Laboratories, Inc. (STL) in Sacramento, California for analysis by reference methods for comparison. Results from the bench-scale tests were used to optimize the testing and analysis processes for the ensuing field demonstration.

2.1.4 Advantages and Limitations of the Technology

DROPEX^{Plus} and EXPRAY^{TM} are demonstrated technologies for identifying a wide variety of explosive compounds in the field. These technologies give a qualitative but rapid indication of whether explosive compounds exist at the testing site and provide information on what type of explosive compounds have been detected. These methods provide an advantage over conventional analysis, which requires sampling, packaging, shipping, and analysis of the sample. DROPEX^{Plus} and EXPRAY^{TM} are rapid techniques and have low rates of false negatives for concentrations above the detection limit. The methods are most useful for screening higher concentrations of NC or NG (above 1,000 mg/kg for bulk material) and identifying hot spots.

Disadvantages of the technologies are that the methods are not quantitative and the identification is not specific for either NC or NG. Some interferences have been observed in the field, causing development of other colors that may mask positives or be misinterpreted as explosives. Detection limits for bulk material analysis by solvent extraction are matrix-dependent and typically in the 40 to 250 mg/kg range for soils and concrete material. The positive color indication for the presence of explosives decreases in intensity near the detection limit, and usefulness for screening levels near the limit may be limited.

One advantage DROPEX^{Plus} has over EXPRAY^{TM} is that the DROPEX^{Plus} reagents are in dropper form and are not as subject to problems due to harsh weather conditions such as extreme cold as the EXPRAY^{TM} reagent spray cans. However, the EXPRAY^{TM} test may be useful for vertical surfaces or applications where dropping the reagents are difficult to perform.

2.2 CRREL COLORIMETRIC METHOD

2.2.1 Technology Development and Application

This method was developed by CRREL, a branch of the USACE Research and Development Center. It was originally published in Development of a Field Screening Method for RDX in Soil (Walsh, 1991). The authors and others have used the method extensively for evaluating soils contaminated with RDX. The method is also in the process of adoption by the EPA as SW-846 Method 8510 (EPA, 2000).

Potential applications for the technology include quantitative field analysis of NC and NG at locations where RDX is not present, as is the case at BAAAP and similar sites.

2.2.2 Process Description

The CRREL RDX Method is a colorimetric quantitative field analytical method for identifying and quantifying RDX and certain other explosives, including pentaerythritol tetranitrate (PETN), high melting explosive, NC, NG, and tetryl. The method involves extracting the soil (or other solid material) with acetone to remove the explosive compounds. The extract is filtered, acidified, and treated with zinc (Zn) dust. Treatment with acid and Zn liberates the nitro groups from the explosive compound(s) as nitrite ions. Nitrite is then quantified using Hach Chemical Company's proprietary NitroVer 3® reagent. This reagent reacts with nitrite to form a pink color whose intensity is proportional to the concentration of nitrite. The absorbance of the treated

extract is measured by a spectrophotometer at a wavelength of 507 nanometers (nm) (see Figure 2).

Figure 2. CRREL Color Development

Color Development

A modification to the CRREL RDX reference method referred to as the modified CRREL method was developed and used in this study to improve the response for NC, which was much lower than that for NG with the original CRREL RDX method. The modification involved the addition of base to the acetone extract to improve the degree of nitrite liberation from NC by alkaline hydrolysis before color development. The modification increased sensitivity and reproducibility for NC consistent with that for NG.

2.2.3 Previous Testing of the Technology

Previous testing of the CRREL technology for NC and NG analysis was performed during the same testing described in Section 2.1.2 for DROPEX^{Plus} and EXPRAY^{TM}.

2.2.4 Advantages and Limitations of the Technology

The advantage of the modified CRREL method lies in its sensitivity, speed, and relatively low cost. The method can be used with training by someone with basic laboratory experience. The method produces a numerical quantitative value for the explosive compounds in the soil based on the quantity of nitrite present.

The method is not specific for NC or NG and provides a response to the total of NG and NC and any other reactive nitro-organic compound; however, since NC and NG are the primary explosives present at the demonstration site, this does not constitute a technical problem.

The method cannot distinguish between NC and NG since the extract treatment destroys both parent compounds, liberating the nitro groups from both. Because there is a difference in weight-related response between NC and NG and only a total response is obtained, samples

containing both NC and NG cannot be quantitatively related with accuracy to either NC or NG unless it is known that the samples contain only NC or only NG. In addition, it is difficult to define the nitro group content for NC in samples, since the molecular formula is not defined and the actual nitro group content varies somewhat depending on the manufacturer's process. This variability contributes to the uncertainty for quantifying NC concentration.

2.3 GC/TID METHOD FOR NG

2.3.1 Technology Development and Application

The use of a field-capable gas chromatography (GC) instrument equipped with a thermionic ionization detection (TID) to analyze for NG in soils was developed and used by researchers from CRREL in 2001. The method is selective for individual determination of NG and other semivolatile explosive compounds. NC is not determined by this method because it is not volatile. The method has been used in limited testing for field sampling and analysis by CRREL developers and was incorporated into this field test for further evaluation.

2.3.2 Process Descriptions

The GC/TID analysis is performed on acetone extracts of sample matrices. Sample extractions are prepared, which may be the same extraction used for the colorimetric testing of EXPRAY^{TM} and DROPEX^{Plus} and the CRREL method. An aliquot of the extract is directly injected onto the GC/TID instrument column using conditions optimized for NG analysis. The GC instrument vaporizes volatile and semivolatile components and passes the vapor through a column using a gas mobile phase. The compounds are separated by interaction with the column surface or surface coating as they pass through the column and emerge separated in time to enter the detector. The detector (TID) is sensitive to compounds containing nitro groups and provides a chromatogram with an enhanced peak area response for each explosive compound at its retention time from the column. The peak area response for NG is related to concentration using standards to prepare a calibration curve.

Typical analysis times are on the order of 5 to 12 minutes per sample. Sample extracts containing high levels of nontarget compounds, such as wood sample extracts, can reduce the analysis sensitivity by loading the injection end of the column with nonvolatile material. Therefore, calibration standard responses must be monitored and, when performance degrades a portion of the injection end of the column, must be removed to regain sensitivity. Figure 3 shows the SRI Instruments, Inc. (SRI) GC/TID.

Figure 3. SRI GC/TID.

2.3.3 Previous Testing of the Technology

Field-capable GC/TID was used successfully to analyze prepared sample extracts for NG and other explosive compounds in soils of CRREL in 2001 (Hewitt et al., 2001) and on soils and mortar fins in 2002 (Hewitt, 2002).

Prior to the field demonstration, a bench-scale study of the DROPEX^{Plus}, EXPRAY^{TM}, CRREL RDX, and GC/TID technologies was conducted by Shaw and results were described in a Bench-Scale Study Report (Appendix C). Uncontaminated soil and building materials (concrete, wood, and wallboard) from the BAAAP site were spiked with known amounts of NG and NG/NC combined at specified levels. Splits of these samples were submitted to STL in Sacramento, California for analysis by reference methods for comparison. The results of the Bench-Scale Study tests showed good general agreement with prepared spike concentrations and the reference method results. Results from the bench-scale tests were used to optimize the testing and analysis processes for the ensuing field demonstration.

2.3.4 Advantages and Limitations of the Technology

The advantages of the GC/TID method are speed, selectivity, sensitivity, and accuracy. The method produces a numerical quantitative value for NG in the sample based on comparison to prepared NG standards with a detection limit of 2 mg/kg. The method may also be used for specific determinations of other semivolatile explosive compounds in the same analysis.

The method, however, cannot detect NC in the sample because it is not volatile and does not chromatograph in the gas phase through the GC/TID column. The analysis requires a GC/TID instrument and associated instrument control and data handling computer, so it is more costly than other field methods and does not lend itself easily to field use without a fixed base facility for power and environmental protection. The analysis requires a chemist with an understanding of chromatography principles and experience in its use as well as knowledge and training on the instrument operation and data handling software, etc.

3.0 DEMONSTRATION DESIGN

3.1 PERFORMANCE OBJECTIVES

The purpose of the demonstration was to evaluate the reliability of field technologies for NC and NG detection in building materials and soil. The technology verification should result in building characterization procedures that may benefit many U.S. Army ammunition plants with similar explosive materials. The implementation of these procedures may also result in substantial savings over conventional remedial investigation techniques of explosive-contaminated buildings. The objectives of the study were as follows:

- *Compound Identification*. Compare the accuracy, feasibility, strengths, and weaknesses of on-site field instrumental and analytical techniques for identifying and measuring NC and NG in or on building materials, foundations, and soils.
- *Compound Quantitation*. Evaluate field data obtained for NC and NG using the quantitative CRREL method and the reference laboratory Methods for the Chemical Analysis of Wastewater (MCAWW) 353.2 for NC and EPA SW-846 Method 8330 for NG using samples of soil, concrete, and wood collected at the BAAAP site.
- *Compound Quantitation*. Evaluate the repeatability of the quantitative analytical results between the ESTCP demonstration methods for NG detection (CRREL method, EPA SW-846 Method 8330, and GC/TID).
- Evaluate the repeatability of qualitative NC detection results of the DROPEX^{Plus} and EXPRAY^{TM} screening methods and quantitative testing using MCAWW 353.2 for NC (i.e., determine the likelihood of false positive or false negative results from the screening methods versus the laboratory quantitative analytical results).
- Evaluate the repeatability of qualitative NG detection results between the DROPEX^{Plus} and EXPRAY^{TM} screening methods and quantitative testing using EPA SW-846 Method 8330 and GC/TID for NG (i.e., determine the likelihood of false positive or false negative results from the screening methods versus the quantitative analytical results).
- Evaluate the repeatability of quantitative analytical results between the ESTCP demonstration methods for NC detection (CRREL method and the MCAWW 353.2 method).

Table 1. Performance Objectives

Type of Performance Objective	Primary Performance Criteria	Expected Performance
Qualitative	False positives	Not more than 5% based on laboratory analysis
	False negatives	Not more than 10% based on laboratory analysis
	False positives and false negatives	Not more than 15% based on laboratory analysis
Quantitative	Method Detection Limit	To be determined
	Agreement with reference laboratory methods for CRREL and GC/TID methods, using statistical correlation methods	Relative percent difference mean not more than 20% and/or linear regression correlation coefficient >0.95

3.2 SELECTION OF TEST SITE(S)

The test sites for performing the technology evaluation were selected using the following criteria:

- Structures were used directly in the manufacture of explosives, specifically NC and/or NG.
- Physical condition of structures exhibited some deterioration and irregularities, particularly in the foundations.
- For purposes of evaluating the overall reliability of the test methods, selected test sites had a strong potential for containing a wide range of NC and NG concentrations. This would include sites where there was significant handling of rocket paste (RP) materials during operations where RP dust would have been generated and where both NC and NG contamination was likely.
- Test sites provided ample locations that likely served as specific accumulators of NC or NG residue. This included soil samples beneath process traffic areas and at drain locations. Concrete core samples were also collected at cracks and slab expansion joints.
- Test sites providing material of the target matrices, wood, soil, and concrete.
- Input from the Shaw Unexploded Ordnance (UXO) Safety Officer (SUXOSO) and areas of interest requested by Army personnel.
- In some cases test sites were prescreened for the presence of explosives using the DROPEX^{Plus} field test kit on surface wipes, and samples were taken in the area of positive indication for NC and NG explosives.

The buildings previously used for the production of RP were selected as fulfilling all these criteria. The activities that occurred in the buildings generated large quantities of dust. The dust has been found in the wooden frame parts of these buildings, and it was anticipated that the dust would be found in or beneath the cracks in the concrete floors. The floors of all five buildings were regularly washed down with water and/or neutralizing solutions, which may also have carried RP compounds into the cracks or may have spilled into the soils under the gutters leading from the buildings. Maps showing the general location of BAAAP and the locations of buildings selected for sampling are included in Appendix B. In addition schematics showing the sampling locations in the buildings are included in the Field Demonstration Report (Appendix D).

3.3 TEST SITE/FACILITY HISTORY/CHARACTERISTICS

The demonstration took place at BAAAP, located on 7,354 acres of land in Sauk County, Wisconsin (Appendix B). BAAAP is one of many inactive Army ammunition plants currently under the control of DoD with transitioning missions in place. The RP area at BAAAP was constructed in the 1944 to 1945 time frame for the manufacture of rocket propellants. RP is used to manufacture a double-based plasticized NC propellant used in rockets. The final propellant contains NC, NG, plasticizers, and burn rate modifiers that are added during various mixing stages of the process. The rocket propellant manufacturing process at BAAAP was performed in three major processing areas: the paste area, the rolls and press area, and finishing area. These areas contain numerous buildings for blending, drying, pressing, and milling propellant. Visible RP was removed from the buildings and burned at the Propellant Burning Ground after BAAAP went on standby status. However, potential accumulation of propellant within, around, and under the buildings' structural foundations has not been addressed. Buildings sampled during the field demonstration along with sample detail information are included in Table 2.

3.4 PHYSICAL SETUP AND OPERATION

3.4.1 On-site Laboratory for Method Testing

A 28-ft mini-mobile laboratory trailer was delivered from Shaw to the BAAAP site on November 29, 2005, for the ESTCP field demonstration. The trailer was powered by a Wagner diesel-powered 100-kilovolt-ampere (kVA) generator with a 240-volt single phase output supplied by a local equipment rental company. The trailer was equipped with a fume hood and small refrigerator. The trailer setup is shown in Figures 4 and 5. Laboratory personnel from the Shaw Technology Development Laboratory (TDL) located in Knoxville, Tennessee, conducted the on-site field analyses on soil, concrete, and wood samples from December 1-19, 2005.

An on-site concrete bunker 100 yards from the mobile laboratory was used for storing samples and breaking concrete cores.

Figure 4. Shaw Lab Trailer and Generator On Site.

Figure 5. Testing Inside Shaw Lab.

3.4.2 Sampling

A total of 104 samples were collected—33 samples of wood, 33 samples of soil, and 37 concrete samples—for test method evaluation during the demonstration. In addition, six concrete expansion joint material samples were separated from concrete cores and were analyzed to investigate NC and NG concentration in this matrix.

Samples for the building investigation demonstration were taken from the following areas, as summarized in Table 2. Additional details are also included in the Field Demonstration Report (Appendix D).

Table 2. Sample Summary.

Building Name (Process Line)	Building ID No.	Wood Samples	Concrete Samples	Soil Samples	Duplicate Samples (A)[1]
Neutralizer House (NG)	6657-02N	2			
Nitrate House (NG)	6657-02I	2			1
Boiling Tub House (NC)	5024	7			1
Pre Dry House (NC, NG)	6709-17	10			1
Powder Storage Pit (NC, NG)	9590	3	1		1
Box Wash House (NC, NG)	1890-01	9	10	3	4
Box Storage Houses (NC, NG)	1885-01, -02, 03		3, 14, 10	0, 25, 5	4
Total Samples Collected		**33**	**37**	**33**	**12**

[1]Duplicate samples were prepared from splits of the parent sample after collection and identified with an (A) added to the sample identification number.

3.4.3 Sample Collection

Wood samples were generated using a cordless drill with a fluted bit. Wood sampling involved drilling multiple (35-50) holes to a depth of approximately one-half inch.

Concrete samples were obtained using a remotely operated hydraulic drill. A water cooled, 3-inch diameter diamond tipped hollow coring bit was used to drill completely through 6- to 8-inch concrete floor slabs.

Surface soil samples were taken by first loosening the soil with a soil coring tool, then collecting the soil with a stainless steel (SS) spoon. Subsurface soil samples were taken from bore holes using long SS spoon tongs after concrete core samples were removed. Many of the subsurface samples required thawing of the frozen ground before soil could be loosened and excavated from the holes. For samples requiring thawing, warm air of no higher than 140°F was blown into each bore hole.

Figure 6. Concrete Core Sampling Team.

Figure 7. Core at Expansion Joint.

The heating of the soil for collection of samples for analysis was performed under the supervision of the senior UXO officer. Material safety and data sheets (MSDS) for NG were consulted prior to applying any heat to the sample locations and the auto-ignition temperature for NG was given as 270°C. The use of 140°F (60°C) air was selected as the upper limit for safety in avoiding decomposition of NG.

3.4.4 Test Sample Preparation

Wood samples, as collected from drilling operations, varied in consistency from fine chips or shavings to 4-inch splinters (thicker than ¼ inch). Samples were chopped using a kitchen blender to reduce piece size to less than approximately ¼ inch. An aliquot of the processed sample was then extracted with acetone using a 1:3 sample weight/solvent volume (w/v) ratio.

Concrete core samples were screened for surface contamination using DROPEX^{Plus} prior to size reduction. Then the top 1-1½-inch cross section and in some cases the side ½-inch longitudinal section next to the seam, if a seam existed, was chipped away with a hammer. Large chips of concrete were crushed using a hammer until all particles were approximately ¼ inch or less. An aliquot of the processed sample was then extracted with acetone using a 1:1 (w/v) ratio.

Soil samples were air dried or oven dried at 40°C and sieved through a 4-inch diameter SS hand strainer with ¼-inch openings. Soil samples were inspected closely for propellant material. Small amounts of recovered propellants were removed from the soil samples. An aliquot of the processed sample was then extracted with acetone using a 1:1 (w/v) ratio.

3.5 ANALYTICAL PROCEDURES

The three methods for identifying and quantifying NC and NG in the field were evaluated on acetone extracts of wood, soil, and concrete material for comparison against off-site laboratory reference method analysis. The methods evaluated were the following:

- DROPEX^{Plus} and EXPRAY^{TM} colorimetric indicator for NC and NG
- CRREL RDX colorimetric field screening method for total NC and NG
- GC/TID portable field GC for NG.

The reference method analyses performed on the sample matrices by STL in Sacramento were the following:

- MCAWW 353.2 for the analysis of NC
- EPA SW-846 8330/8332 for the analysis of NG.

Copies of the methods may be found in Appendix B, Experimental Methods Supporting the Experimental Design (not used), of the ESTCP Demonstration Plan (Shaw, 2004).

3.5.1 Reference Method MCAWW 353.2 Methodology

MCAWW 353.2 (EPA, 1983) is a colorimetric method used to determine nitrate, nitrite, each singularly or in combination. The method has been adapted for NC determination in the form of nitrate plus nitrite in waters, soils, and sediments. The method is specific for the analysis of NC in a sample. The method pre-extraction steps with methanol and water remove inorganic forms of nitrate and nitrite as well as nitroglycerin from the sample. NC is insoluble in these solvents and is subsequently removed from the solid matrix in the acetone solvent extraction. The acetone extract is then hydrolyzed to remove NC compound nitro groups and produce inorganic nitrite and nitrate ions. The nitrate ions are then reduced to nitrite with a cadmium (Cd) column and the total nitrite content is quantified using a spectrophotometer after reaction with a reagent to produce a highly colored species that is a pink-red color.

3.5.2 Reference Method EPA SW-846 8330/8332 Methodology

EPA SW-846 Methods 8330/8332 (EPA, 1995; EPA, 1998) are high-performance liquid chromatography (HPLC) methods for the extraction and detection of explosive residues in

waters, soils, and sediments. Samples are analyzed on an HPLC with a reverse-phase column at an ultraviolet (UV) detection of 250 nm. Solid samples are air-dried, ground, sieved through a 30-mesh screen, extracted with acetonitrile, treated with calcium (Ca) chloride solution, filtered, and the extracts are analyzed by HPLC.

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4.0 PERFORMANCE ASSESSMENT

4.1 PERFORMANCE DATA

Demonstration results for each of the technologies that were evaluated are discussed in depth in the "Draft Field Demonstration Report, Applied Innovative Technologies for Characterization of Nitrocellulose and Nitroglycerin Contaminated Buildings and Soils" (Appendix D). Additional data are found in the initial "Bench-Scale Study Report, Verification of Field Test Methods for Nitrocellulose- and Nitroglycerine-Spiked Samples of Soil and Building Materials" (Appendix C).

4.1.1 DROPEX^{Plus} and EXPRAY^{TM}

DROPEX^{Plus} and EXPRAY^{TM} were found to have matrix dependent detection limits for acetone extract analyses. This was determined in the bench-scale study and discussed in detail in the Bench-Scale Study Report (Appendix C). The results are summarized in Table 3. Results from the field test study showed that neither NG nor NC was stable on the concrete matrix due to hydrolytic degradation because of the alkaline nature of the matrix. It was further shown that detection of these compounds was a function of the form of the contamination, i.e., pieces or in solution, and the length of time on the matrix. Hence, after a period of time on the order of hours to days on concrete matrix, neither NG nor NC may be detectable due to degradation. The values for detection on concrete matrix in Table 3 were obtained on samples that were spiked and extracted in a short amount of time between being spiked and do not represent meaningful values for environmental concrete samples.

EXPRAY^{TM} was effective in detecting NC and NG in the soil and wood matrices with results consistent with the STL reference methods as long as concentrations were above detectable limits. DROPEX^{Plus} did not meet the performance metrics for wood or soil probably due to lower detection limits, which involved more samples with concentrations near the detection limit where variability in method performance is the highest and has the greatest impact.

Table 3. Bench Test Detectable Limits DROPEX^{Plus}/EXPRAY^{TM}.

Spike Material	EXPRAY^{TM} Detectable Limit mg/kg	DROPEX^{Plus} Detectable Limit mg/kg
Soil Extracts		
NC	250	100
NG	40	40
Combined NC/NG	250/25	250/25
Wood Extracts		
NC	2500	250
NG	250	80
Combined NC/NG	4000/400	250/400
Concrete Extracts[a]		
NC	250	250
NG	ND	ND
Combined NC/NG	1000/100	250/25

NG – nitroglycerine; NC – nitrocellulose; mg/kg – milligrams per kilogram; ND – not determined, no detection

[a]Detection limits measured for concrete were obtained on samples that were extracted within a short amount of time after being spiked and do not represent meaningful values for environmental samples because of degradation of NC and NG that occurs in a matter of hours to days on the matrix.

4.1.2 CRREL Results for Total NC and NG

The original CRREL RDX method gave a relatively low response for NC compared to NG that was easily impacted by matrix interferences. Analysis of the wood matrix samples could not be performed because of low analyte response. Analysis of the soil and concrete samples were able to be performed by the method. The comparisons of the results for the CRREL RDX method versus the total STL reference method results are shown in Figure 8 for soil samples and Figure 9 for concrete samples.

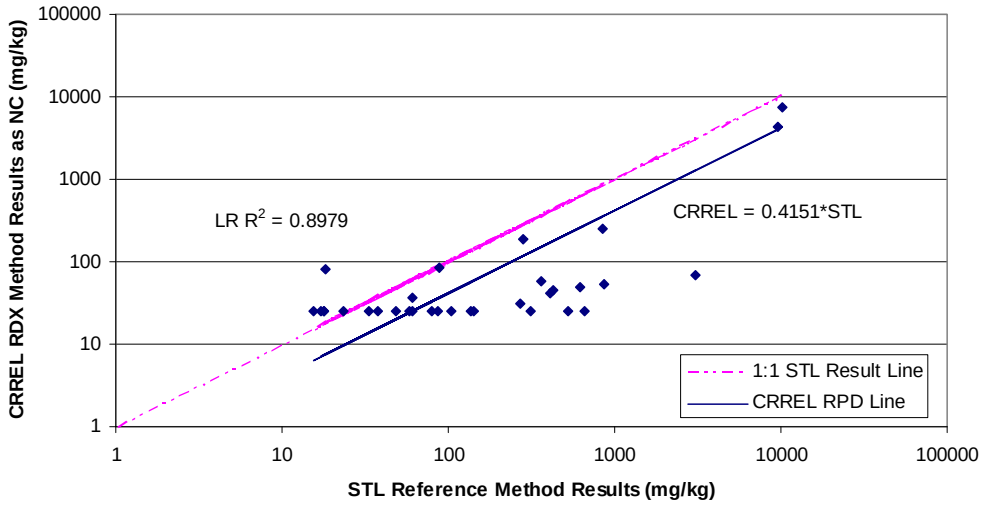

Figure 8. CRREL RDX Results for NC/NG on Soil Versus STL Reference Method Results.

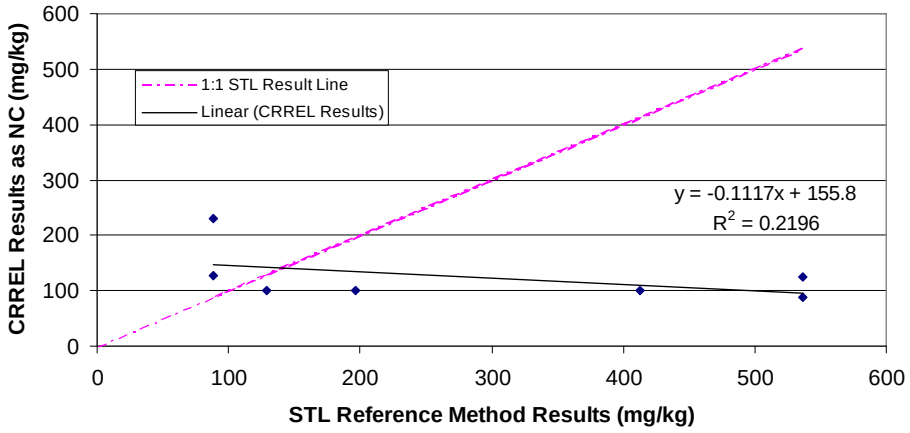

Figure 9. CRREL Method Results for NC/NG on Concrete Versus STL Reference Method Results.

Modifications to the CRREL RDX procedure greatly increased the method response for NC and retained the response for NG. The increase in response made the method more robust for NC analysis and allowed analysis of NC on all three sample matrices. The detection limit for NC

analysis by the modified CRREL method is also in the range of an order of magnitude lower than that for the original CRREL RDX method. Details of the method modifications and development are included in the Field Demonstration Report (Appendix D).

Figures 10 and 11 show the correlation of results for wood and soil sample analyses by the modified CRREL method compared to those from the STL reference methods from the field demonstration.

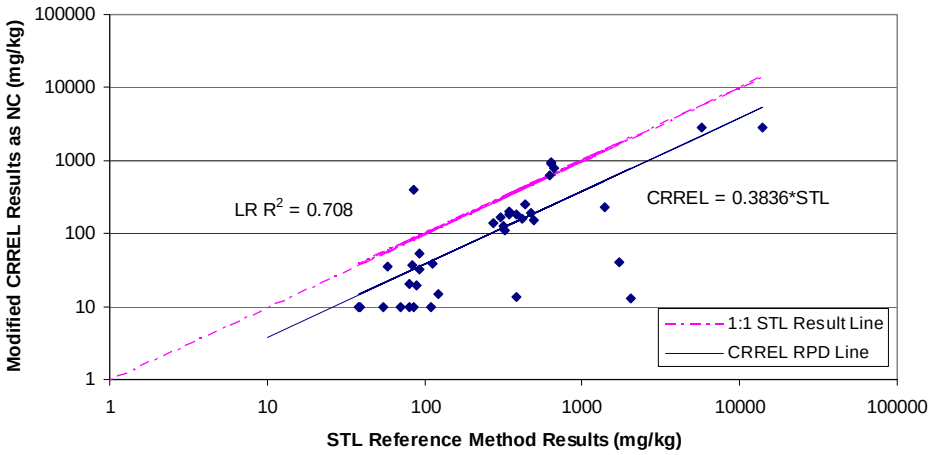

Figure 10. Modified CRREL Results for NC/NG on Wood Versus STL Reference Method Results.

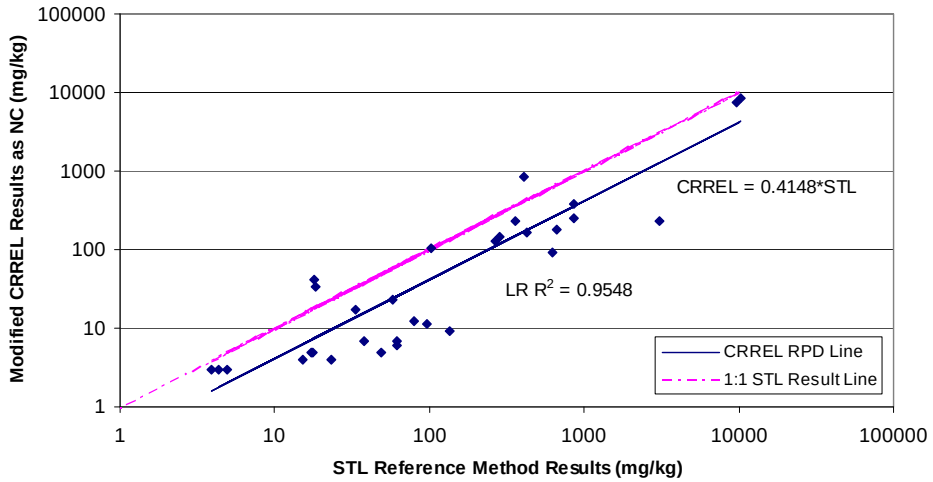

Figure 11. Modified CRREL Results for NC/NG on Soil Versus STL Reference Method Results.

Figure 12 shows the comparison for the results obtained for soil sample extract analyses using the modified CRREL method versus the original CRREL RDX method and illustrates general agreement between the two methods.

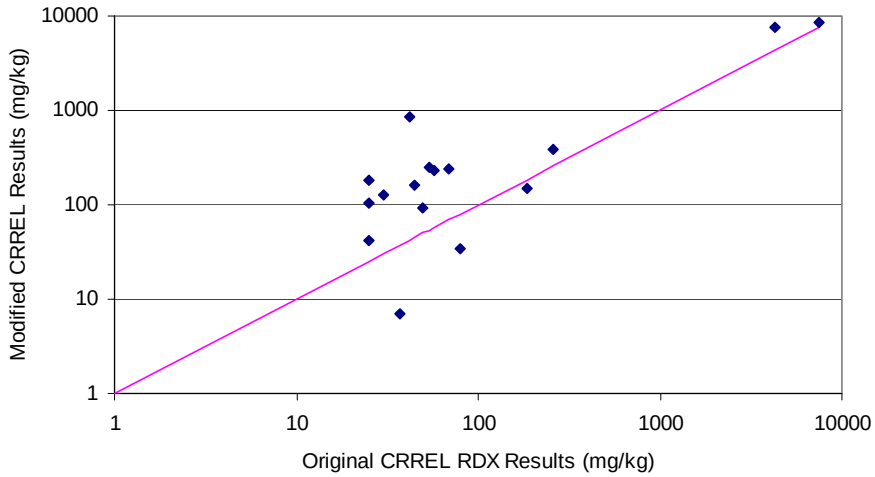

Figure 12. Comparison of Modified CRREL Test Results Versus Original CRREL Test Results on Soil Extracts.

The CRREL RDX method detected NC/NG above the detection limit in only two of the concrete samples, one sample and its duplicate at NC concentrations of 124 mg/kg and 128 mg/kg (ND level was 100 mg/kg as NC). Analysis using the modified CRREL method was performed on the original sample in duplicate. The modified CRREL method analysis detected NC/NG at an NC concentration of 87 mg/kg and 230 mg/kg. These results were consistent with the original CRREL RDX results but do reflect some variation most likely due to the nonhomogeneous nature of the sample matrix.

Tests conducted with NC on concrete showed that recovery of NC from the matrix was a function of both time and the manner in which NC was deposited on the matrix. These results were attributed to decomposition of NC by the concrete matrix due to its alkaline nature in a similar manner as to what was concluded for NG with spiked matrix samples in the Bench-Scale Study Report (Appendix C).

Compound concentration metrics with respect to the relative percent difference (RPD) values between the CRREL method and the reference laboratory methods were not met by the CRREL methods with any of the three matrices. CRREL results were consistently biased low in comparison to the STL reference method results. STL Method 353.2 results were believed to be biased high due to matrix interference or contamination phenomenon similar to what affected method blanks and results in the bench-scale study. The RPD between CRREL and STL results ranged from 42.2 to 89.1 percent. Performance metrics for concrete samples were limited by the number of positive results obtained by the CRREL methods.

There was also considerable scatter in the RPD values for the method result comparisons. This was attributed to nonhomogeneous sample material and sources of contamination.

Contamination of building materials (concrete and wood) was likely concentrated on exposed surfaces of the material. The sample size reduction to a particle size of about ¼ inch was not enough to provide sufficient distribution for uniform sampling. Soil samples also contained pieces of propellant material that made preparing a homogeneous sample difficult.

4.1.3 GC/TID Results for NG

GC/TID analysis of NG was sensitive; a detection limit of 2 mg/kg, which was comparable to the reference method, was observed for soil and concrete. Wood had a slightly higher detection limit of 5 mg/kg due to increased solvent volume used in sample extraction. Analyte detection performance metrics for NG were met for all three matrices with <5% false negatives and <10% positives; however, analyte concentration performance metrics were not met. Performance metrics for concrete and soil samples were limited by the number of positive results obtained. The comparison of GC/TID results to the STL reference method results for wood samples is shown in Figure 13.

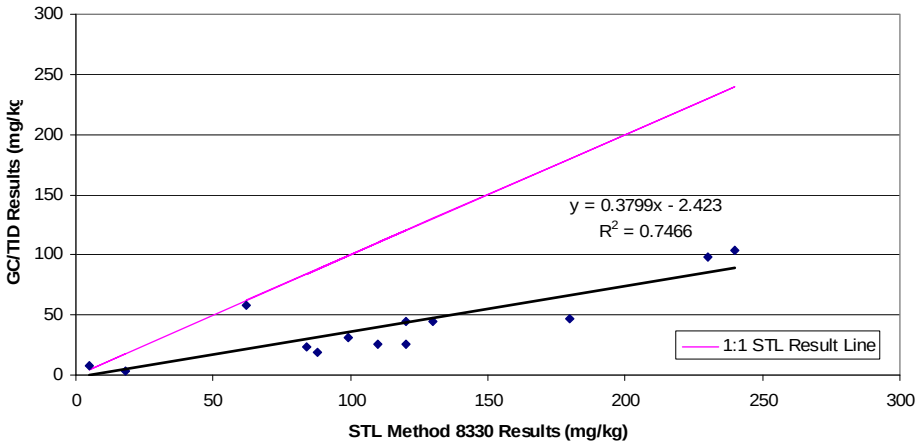

Figure 13. GC/TID Results for NG on Wood Versus STL Method 8330 Results.

4.2 PERFORMANCE CRITERIA

The effectiveness of the demonstration was evaluated by confirming the performance of each of the technologies. Performance confirmation was based on comparison of analyte detection and quantitative results to fixed-base laboratory analytical results from reference methods. Comparisons of analysis results were performed taking into account different method detection limits and used a defined handling of nondetect results. Statistical measures of quantitative results were calculated for comparison. A detailed discussion of data assessment methods is provided in the Draft Field Demonstration Report (Appendix D)

System performance was measured in definitive ways to the extent practical for both primary and secondary criteria, as initially identified in the Demonstration Plan (Shaw, 2004). Exceptions to the work plan were as follows: no asbestos-containing material (ACM) was tested due to safety issues related to crushing of ACM, and Raman spectroscopy was not used due to safety issues related to heat generation noted during the bench-scale testing.

The performance evaluation is presented for each of the matrices in Tables 4, 5 and 6.

Table 4. Wood Samples—Performance Evaluation against Primary and Secondary Criteria.

Performance Criteria	Expected Performance Metric (pre-Demo)	Performance Confirmation Method	Actual Performance (post-Demo)
Primary Criteria			
Compound Identification	NMT 5% false negatives NMT 10% false positives (applies to DROPEX^{Plus} and EXPRAY^{TM})	Confirm by laboratory analysis Data to be evaluated on agreement of detection	• DROPEX^{Plus} field method false negatives=16.2% • EXPRAY^{TM} field method false negatives= 0% • DROPEX^{Plus} field method false positives= 5.4% • EXPRAY^{TM} field method false positives= 13.5% Field methods do not meet specified criteria.
Compound Concentration	RPD NMT 20% and/or correlation coefficient ≥ 0.95 (applies to CRREL and GC/TID)	Confirm by laboratory analysis Data are evaluated on agreement of detection and concentration	• Modified CRREL field method RPD=89.1 • GC/TID field method RPD= 48.7 • Modified CRREL field method LR R value=0.7080 • GC/TID field method LR R value= 0.7466 Field Methods do not meet specified criteria.
Reliability	Achieve identification and quantitation requirements in multiple locations and conditions	Confirm by laboratory analysis	• GC/TID—wood does not pass RPD criteria. • CRREL/modified CRREL does not meet specified criteria.
Ease of Use	Reduced or constant crew size Level of technical training required Need for special assistance or training during project Calibration and maintenance able to be performed by operating crew	Experience from demonstration	• EXPRAY^{TM} and DROPEX^{Plus} is easy to use with little specialized training and equipment. • CRREL requires a moderate level of training in regard to matrix. • GC/TID requires specialized training.
Maintenance	Percent downtime when operations are scheduled Routine maintenance required Specialized personnel or equipment for maintenance activities	Experience from demonstration	DROPEX^{Plus} and EXPRAY^{TM} do not use equipment that requires maintenance or repair. CRREL does not use equipment that requires maintenance or repair. GC/TID maintenance and repair can be performed by trained GC analyst with 5-10% downtime.

Table 4. Wood Samples—Performance Evaluation against Primary and Secondary Criteria (continued)**.**

Performance Criteria	Expected Performance Metric (Pre-Demo)	Performance Confirmation Method	Actual Performance (Post-Demo)
Secondary Criteria			
Versatility	Use conditions and ease of use under a variety of site conditions	Experience from demonstration	DROPEX^{Plus} and EXPRAY^{TM} can be used under a wide variety of site conditions. CRREL can be used under a wide variety of site conditions. GC/TID requires a relatively stable environment with temperatures within 70° ±20°F. All equipment is portable, light, and easily transported.
Hazardous Materials	Volume of hazardous materials generated by project operations Number of waste streams requiring characterization and disposal	Experience from demonstration	• Minimal hazardous materials were generated during project. • Remaining acetone extracts were returned to Shaw Knoxville Laboratory for disposal as hazardous waste.
Process Waste	Amount of investigative-derived waste generated by project operations.	Experience from demonstration	Each sample for any of the analytical methods produced contact waste that is disposable to trash consisting of a 2-ounce sample bottle, a 20-mL extract vial, a disposable syringe and 1-2 disposable syringe filters. The CRREL method produced an additional 10-mL disposable resin tube, 1-2 disposable syringes, 1-2 syringe filters, and 1-2 glass vials for processed sample fractions. Aqueous solutions from CRREL method sample processing (10-30 mL) are disposable to municipal drain. For any of the methods, acetone extracts of samples are prepared (60-100 mL per sample). These may be evaporated in a fume hood, depending on local air permits, and the residue may be disposed of as minimal contact trash or as hazardous solid waste. Alternatively, the acetone sample extracts may be disposed of as a hazardous solvent.

Notes:
NMT = not more than
RPD = Relative Percent Difference

Table 5. Soil Samples—Performance Evaluation Against Primary and Secondary Criteria.

Performance Criteria	Expected Performance Metric (Pre-Demo)	Performance Confirmation Method	Actual Performance (Post-Demo)
Primary Criteria			
Compound Identification	NMT 5% false negatives NMT 10% false positives (Applies to DROPEX^{Plus} and EXPRAY^{TM})	Confirm by laboratory analysis Data to be evaluated on agreement of detection	• DROPEX^{Plus} field method false negatives=10.8% • EXPRAY^{TM} field method false negatives= 2.7% • DROPEX^{Plus} field method false positives= 16.2% • EXPRAY^{TM} field method false positives= 8.1% DROPEX^{Plus} does not meet criteria. EXPRAY^{TM} does meet criteria.
Compound Concentration	RPD NMT 20% and/or correlation coefficient ≥ 0.95 (applies to CRREL and GC/TID)	Confirm by laboratory analysis Data evaluated on agreement of detection and concentration	• Modified CRREL field method RPD=82.7 • GC/TID field method RPD= -12.9 • Modified CRREL field method R value=0.9548 • GC/TID field method LR R value= 0.2566
Reliability	Achieve identification and quantitation requirements in multiple locations and conditions	Confirm by laboratory analysis	• GC/TID—soil and concrete quantitation are not confirmed because of absence of NG compound. • CRREL/ Modified CRREL does not meet specified criteria
Ease of Use	Reduced or constant crew size Level of technical training required Need for special assistance or training during project Calibration and maintenance able to be performed by operating crew	Experience from demonstration	• EXPRAY^{TM} and DROPEX^{Plus} is easy to use with little specialized training and equipment. • CRREL requires a moderate level of training in regard to matrix. • GC/TID requires specialized training.
Maintenance	Percent downtime when operations are scheduled Routine maintenance required Specialized personnel or equipment for maintenance activities	Experience from demonstration	DROPEX^{Plus} and EXPRAY^{TM} do not use equipment that requires maintenance or repair. CRREL does not use equipment that requires maintenance or repair. GC/TID maintenance and repair can be performed by trained GC analyst with 5-10% downtime.

Table 5. Soil Samples—Performance Evaluation Against Primary and Secondary Criteria (continued)**.**

Performance Criteria	Expected Performance Metric (Pre-Demo)	Performance Confirmation Method	Actual Performance (Post-Demo)
Secondary Criteria			
Versatility	Use conditions and ease of use under a variety of site conditions	Experience from demonstration	DROPEX^{Plus} and EXPRAY^{TM} can be used under a wide variety of site conditions. CRREL can be used under a wide variety of site conditions. GC/TID requires a relatively stable environment with temperatures within 70° ±20°F. All equipment is portable, light, and easily transported
Hazardous Materials	Volume of hazardous materials generated by project operations Number of waste streams requiring characterization and disposal	Experience from demonstration	• Minimal hazardous materials were generated during project. • Remaining acetone extracts were returned to Shaw Knoxville Laboratory for disposal as hazardous waste.
Process Waste	Amount of investigative-derived waste generated by project operations	Experience from demonstration	Each sample for any of the analytical methods produced contact waste that is disposable to trash consisting of a 2-ounce sample bottle, a 20-mL extract vial, a disposable syringe, and 1-2 disposable syringe filters. The CRREL method produced an additional 10-mL disposable resin tube, 1-2 disposable syringes, 1-2 syringe filters, and 1-2 glass vials for processed sample fractions. Aqueous solutions from CRREL method sample processing (10-30 mL) are disposable to municipal drain. For any of the methods, acetone extracts of samples are prepared (20-50 mL per sample). These may be evaporated in a fume hood, depending on local air permits, and the residue may be disposed of as minimal contact trash or as hazardous solid waste. Alternatively, the acetone sample extracts may be disposed of as a hazardous solvent.

Notes:
NMT = not more than
RPD = Relative Percent Difference

Table 6. Concrete Material—Performance Evaluation Against Primary and Secondary Criteria.

Performance Criteria	Expected Performance Metric (Pre-Demo)	Performance Confirmation Method	Actual Performance (Post-Demo)
Primary Criteria			
Compound Identification	NMT 5% false negatives NMT 10% false positives (applies to DROPEX^{Plus} and EXPRAY^{TM})	Confirm by laboratory analysis. Data will be evaluated on agreement of detection.	• DROPEX^{Plus} field method false negatives=2.4% • EXPRAY^{TM} field method false negatives= 4.9% • DROPEX^{Plus} field method false positives= 2.4% • EXPRAY^{TM} field method false Positives= 0% DROPEX^{Plus} and EXPRAY^{TM} meet performance criteria.
Compound Concentration	RPD NMT 20% and/or correlation coefficient ≥ 0.95 (applies to CRREL and GC/TID)	Confirm by laboratory analysis. Data are evaluated on agreement of detection and concentration	• CRREL field method RPD=45.9 • GC/TID field method RPD= -4.43 • CRREL field method R value=0.0894 • GC/TID field method LR R value= NC insufficient data points • CRREL and GC/TID fail to meet specified criteria.
Reliability	Achieve identification and quantitation requirements in multiple locations and conditions	Confirm by laboratory analysis	• GC/TID—soil and concrete quantitation not confirmed because of absence of NG compound. • CRREL performance not confirmed
Ease of Use	Reduced or constant crew size Level of technical training required Need for special assistance or training during project Calibration and maintenance able to be performed by operating crew	Experience from demonstration	• EXPRAY^{TM} and DROPEX^{Plus} is easy to use with little specialized training and equipment. • CRREL requires a moderate level of training in regard to matrix. • GC/TID requires specialized training.
Maintenance	Percent downtime when operations are scheduled Routine maintenance required Specialized personnel or equipment for maintenance activities	Experience from demonstration	DROPEX^{Plus} and EXPRAY^{TM} do not use equipment that requires maintenance or repair. CRREL does not use equipment that requires maintenance or repair. GC/TID maintenance and repair can be performed by trained GC analyst with 5-10% downtime.

Table 6. Concrete Material—Performance Evaluation Against Primary and Secondary Criteria (continued)**.**

Performance Criteria	Expected Performance Metric (Pre-Demo)	Performance Confirmation Method	Actual Performance (Post-Demo)
Secondary Criteria			
Versatility	Use conditions and ease of use under a variety of site conditions.	Experience from demonstration	DROPEX^{Plus} and EXPRAY^{TM} can be used under a wide variety of site conditions. CRREL can be used under a wide variety of site conditions. GC/TID requires a relatively stable environment with temperatures within 70° ±20°F. All equipment is portable, light, and easily transported.
Hazardous Materials	Volume of hazardous materials generated by project operations. Number of waste streams requiring characterization and disposal	Experience from demonstration	• Minimal hazardous materials were generated during project. • Remaining acetone extracts were returned to Shaw Knoxville Laboratory for disposal as hazardous waste
Process Waste	Amount of investigative-derived waste generated by project operations.	Experience from demonstration	Each sample for any of the analytical methods produced contact waste that is disposable to trash consisting of a 2-ounce sample bottle, a 20 mL extract vial, a disposable syringe and 1-2 disposable syringe filters. The CRREL method produced an additional 10-mL disposable resin tube, 1-2 disposable syringes, 1-2 syringe filters, and 1-2 glass vials for processed sample fractions. Aqueous solutions from CRREL method sample processing (10-30 mL) are disposable to municipal drain. For any of the methods, acetone extracts of samples are prepared (20-50 mL per sample). These may be evaporated in a fume hood, depending on local air permits, and the residue may be disposed of as minimal contact trash or as hazardous solid waste. Alternatively, the acetone sample extracts may be disposed of as a hazardous solvent.

Notes:
NMT = not more than
RPD = Relative Percent Difference

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4.3 DATA ASSESSMENT

4.3.1 DROPEX^{Plus} and EXPRAY^{TM} Test Kits

The DROPEX^{Plus} and EXPRAY^{TM} results were recorded as either a positive (+) or negative (-) test response. In some cases, sample concentrations near the detectable limit for the method gave a positive result that was only faintly discernable, but in general, the test response was increasingly more intense as the test NC or NG concentration increased above the detectable limit. Detectable limits of spiked NC and NG material varied for each test matrix. A major portion of the false positive and false negative results were obtained for tests that were near the technology detection limits, and sample nonhomogeneity may have contributed to the false indications.

The demonstration field personnel preferred DROPEX^{Plus} during the sample collection screening due to the extremely cold temperatures (sub 0) at the BAAAP site in December. The EXPRAY^{TM} spray cans did not perform as well in the extreme conditions encountered outdoors and were not used by the sample collection team.

The DROPEX^{Plus} and EXPRAY^{TM} test kits require little training to use on sample wipes and the results are easily interpreted. On sample extracts, some training will likely be required on sample preparation procedures.

4.3.2 CRREL Methodology

It is Shaw's opinion that the original CRREL RDX method is not appropriate for analysis of NC due to incomplete reaction of NC with the method reagents and resulting low and inconsistent response. The method is usable for the analysis of NG on the matrices tested. The modified CRREL method developed in this study is suitable for analysis of either NG or NC or mixtures of NG and NC. Neither CRREL method is specific to NG or NC, and both provide a response to the total of NG and NC. The modified CRREL method, however, produces a similar response for each analyte such that the total analytical result can be expressed nearly equivalently as NG, NC, or a mixture of NG and NC within 75% to 130% accuracy.

The CRREL results were consistently biased low in comparison to the STL reference method 353.2 results. This affected both the number of false negatives for the CRREL method and the RPD between the results for the two methods. The RPD between CRREL and STL results ranged from 42.2 to 89.1%. For concrete samples, there were a limited number of positive results obtained by the CRREL methods. The STL method 353.2 results appeared to be biased high due to matrix interference or contamination phenomenon similar to what affected method blanks and clean background matrix analyses in the bench test and field demonstration. NC was detected in all of the samples analyzed by the STL method 353.2.

There was also considerable scatter in the RPD values for the CRREL method result comparisons. This was attributed to nonhomogeneous sample material and sources of contamination. Soil samples in particular contained pieces of propellant material that made preparing a homogeneous sample difficult.

The CRREL method requires a person experienced in laboratory techniques and trained on the spectrometer operation and method specifics.

4.3.3 GC/TID Method

In general, reliability of the GC/TID ability to detect NG on the building materials was consistent with the reference Method 8330. Wood matrix sample set was the only one that provided enough positive results for a meaningful quantitative method comparison. The GC/TID results from this set were biased low compared to the reference Method 8330 results, and the RPD was outside the performance metric for agreement. The wood matrix provides an organic rich background that may have provided a positive interference for the STL method; however, both methods are subject to matrix interference effects. The bench-scale study demonstrated good GC/TID results agreement with NG spike concentrations on clean background matrix samples.

The GC/TID method requires a person experienced in GC techniques and trained on the instrument operation and method specifics.

4.4 TECHNOLOGY COMPARISON

Table 7 lists the various demonstration technologies tested and which technologies experienced successful validations (i.e., met a priori performance metrics) and which technology demonstrations remain uncompleted due to lack of necessary data. Also shown are the primary validation criteria that were failed if the validation was not successful as well as qualifying text or clarification applicable to the tested technology demonstration results.

Table 7. Demonstration Technologies Validation Summary.

Technology	Validation Success	Primary Validation Criteria Failure	Comment
DROPEX^{Plus}	Wood—No Soil—No Concrete—Yes	Wood—High FN Soil—High FN & FP Concrete—NA	Wood and soil—More sensitive than EXPRAY^{TM} and there were a large number of results near DL where results are variable
EXPRAY^{TM}	Wood—No Soil—Yes Concrete—Yes	Wood—High FP Soil—NA Concrete—NA	Wood—FP at 13.9%, just over 10% limit criteria
CRREL RDX	Wood—NA Soil—No Concrete—No	Wood—All Soil—High RPD; Low CC Concrete—High RPD; Low CC	Wood—No NC response, matrix interference Soil & concrete—Results biased low versus reference; possible high bias by reference
Modified CRREL	Wood—No Soil—No Concrete—No	Wood—High RPD; Low CC Soil—High RPD Concrete—High RPD; Low CC	Wood and soil—Results biased low versus reference; possible high bias by reference; high CC for soil Concrete—Insufficient data
GC/TID	Wood—No Soil—No Concrete—NA	Wood—High RPD; Low CC Soil—Low CC Concrete—NA	Wood—Results biased low versus reference; possible high bias by reference Soil and concrete—Insufficient positive results

FN = False negatives FP = False positives RPD = Relative percent difference from STL reference method results
CC – Linear regression correlation coefficient for results plotted against STL reference method results DL = Detection limit

5.0 COST ASSESSMENT

5.1 COST REPORTING

Project costs were tracked and are summarized in Table 8. The apportioned demonstration costs of on-site sampling and on-site analyses for; DROPEX^{Plus} and EXPRAY^{TM} testing, CRREL Method testing, and GC/TID method testing are provided on Tables 9 and 10. Some of Shaw's costs are apportioned between the tasks based on estimates of percentage use/effort for each task. The costs for off-site reference method analyses by STL are isolated in Table 11. Some costs for shipping and data validation were apportioned to the STL costs based on estimates of use/effort for these activities. The unit cost per sample or sample location is provided for each activity.

The actual costs for implementation of the field technologies are expected to be lower than those for the demonstration due to factors related to technology development and evaluation, as discussed below.

The ESTCP project costs from November 2005 through March 2006 are directly related to the field demonstration and associated administrative activities and can be divided into five cost categories:

1. On-site sampling
2. On-site sample analysis
3. Off-site sample analysis and data validation
4. Off-site method development and sample reanalysis
5. Administration and reporting.

Administrative and reporting costs totaled $53,035 and are not included in Table 8. The costs for the field demonstration activities that are included in Table 8 totaled $176,264. The total project cost for the field demonstration, including administrative and reporting activities, was $229,299.

Sampling costs of $37,229 included sample design and planning, equipment fabrication and modification (remote operated concrete drill and sample crusher), materials and supplies related to sampling activities, equipment rental, personnel travel costs, and labor for sampling activities. These costs, shown in Table 8 and isolated in Table 9, can be used for estimating sampling costs, but they were affected by the subfreezing temperatures, which necessitated special efforts to thaw soil for sampling beneath the concrete slab at concrete core sampling sites. A water-cooled, diamond-tipped, hollow coring bit was used to drill through concrete floor slabs. This was chosen as a method to provide safe access to subslab samples. This method was expensive and likely caused some disturbance to the sample due to the water used to cool the drill bit. Alternative methods of obtaining these samples should continue to be investigated. Costs related to concrete cutting will also be affected by the thickness and strength of the concrete slab. There were 103 sample locations and the average sampling cost per location was $361.

On-site sample analysis costs for a total of $61,808 included those for planning, materials, and supplies related to analyses, laboratory trailer, and generator rental as well as associated delivery charges, generator fuel costs, personnel travel costs, shipping charges for equipment and supplies during mobilization and demobilization, and labor for sample preparation and analysis. The

costs are apportioned between the three analytical method technologies—EXPRAY™ /DROPEX^{Plus}, GC/TID, and CRREL—and are shown in Table 10. The estimated cost breakdown for each method technology is $10,493 for EXPRAY™/DROPEX^{Plus}, $24,078 for GC/TID, and $27,237 for CRREL. These costs are for the analysis of the 115 samples, 103 field samples, and 12 field sample duplicates. DROPEX^{Plus} was also used to analyze 36 of the concrete core surfaces so the total number of samples analyzed by EXPRAY™/DROPEX^{Plus} was 151. The average cost for on-site analysis of the samples by all technologies was $516 per sample.

Off-site sample analysis costs of $22,830, shown in Table 8 and detailed in Table 11, included those for sample shipping, unit price charges for samples analyzed by STL, and costs for data validation. The unit cost for off-site analysis of the samples by both reference methods was $199 per sample. What are not included are labor costs for sample shipment and administrative activities as well as for sample preparation activities, which are included in on-site analytical charges. Sample preparation that was necessary for both on-site and off-site analyses was performed on-site during the analysis efforts and the costs are difficult to separate out accurately; however, they are estimated to be 15% of the estimated on-site analytical labor costs of $33,081 or approximately $4,960. The off-site analysis costs plus the estimated sample preparation cost gives a total estimated cost of $27,790 for off-site analysis or $242 per sample, if only off-site analyses were performed, because sample preparation would still be required.

There was a significant effort expended after the on-site field demonstration at the TDL in Knoxville, Tennessee, for CRREL RDX method development/modification and sample re-analysis that would not be needed for routine use of the developed method. It was felt that the labor expended on site is a good estimate of the labor needed to complete the analysis of the samples collected for the field demonstration using the EXPRAY™/DROPEX^{Plus}, GC/TID, and the developed modified CRREL field methods. Therefore, the estimated off-site method development costs were not included in the costs for on-site analytical work. An estimate of the labor and materials cost for off-site CRREL method development has been separated from the on-site work and shown in a separate column in Table 8.

5.2 COST COMPARISONS TO CONVENTIONAL AND OTHER TECHNOLOGIES

The STL costs for the demonstration samples of $27,790 (includes $4,960 cost for sample preparation), or $242 per sample, can be compared to the on-site analytical costs to assess cost-effectiveness for on-site analyses. The on-site analysis costs were $516 per sample for all the field methods. For more direct comparison to the off-site cost, the cost for only GC/TID and CRREL method analyses was $446 per sample, approximately twice the cost for off-site analysis. This comparison does not include administrative costs previously mentioned or the cost for expedited turnaround of results from the off-site laboratory that would be incurred to get a more direct comparison to the on-site field analysis. On-site analysis typically generates results the same day or within 24-48 hours. The off-site analyses were performed by STL with a 3-week turnaround time for results. STL typically charges a 50% to 100% surcharge for results within a 24- to 48-hour turnaround time. However, there is typically a 24-hour delay due to overnight shipping, so it is difficult for an off-site laboratory to duplicate the turnaround time for results that an on-site laboratory can provide.

Another factor affecting the cost that should be considered for cost comparison is the experience level of the analysts used for field method analysis. Since this was a method evaluation and included analytical method development, the experience level and associated pay rate for analysts were higher than what would typically be used for field work using established analytical procedures.

It is difficult to get a clear cost comparison for the EXPRAY^{TM}/DROPEX^{Plus} and CRREL methods to the off-site reference method analyses because the results for the methods are not equivalent. The CRREL method provides a total for NC and NG while EXPRAY^{TM} and DROPEX^{Plus} are not quantitative and the MCAWW 353.2 reference method only quantifies NC. Probably the best overall comparison is the total cost for the GC/TID and CRREL analyses, which provide separate results for NG and NC (by difference between the CRREL total NC and NG result and the GC/TID NG result) versus the cost for both the off-site STL reference method analyses that provides separate results for NC and NG, as was discussed above. In addition however, the GC/TID method and the STL 8330/8332 method both provide quantitative results for NG only and the estimated costs for these analyses were $24,078 ($209 per sample) for GC/TID and approximately $13,000 or $116 per sample for Method 8330/8332 (STL). The on-site GC/TID cost was approximately twice that for the off-site laboratory analysis and is consistent with the former comparison, but again lacks the mentioned considerations for a more valid comparison.

It is felt that the costs for on-site analyses versus rapid turnaround off-site analyses would be comparable under routine operation and that the results obtained (using the GC/TID and the modified CRREL method) would be comparable. However, the on-site analysis capability offers convenience, more flexibility, and most likely an advantage in turnaround of analytical results. In many cases, on-site analyses can be performed with results turnaround within a few hours.

Table 8. Overall Demonstration Costs.

Cost Category	SubCategory	Details	Field Sampling On Site	On-Site Field Method Analysis	Off-Site CRREL Method Development	Off-Site STL Reference Method Analyses	Total Actual Demonstration Costs (Includes Shaw Costs)
Start-up costs	Site characterization	N/A					
	Mobilization	Project planning	$5,000	$7,500			$12,500
		Project coordination					
		Personnel travel to site	$5,845	$10,000			$15,845
		Equipment travel to site					
		Shipping costs	$483	$800			$1,283
Capital costs	Capital equipment purchase	N/A					
	Ancillary equipment purchase	N/A					
	Modifications	Concrete drill	$940				$940
	Structures installation	N/A					
	Engineering	N/A					
Operating costs	Capital equipment rental	Shaw rental – laboratory trailer, misc		$1,208			$1,208
	Ancillary equipment rental	Trailer generator and fuel		$1,141			$1,141
		Phone services	$450	$496			$946
	Supervision	Salary					
		Travel					
		Per diem					
	Operator laboratory	Salary	$24,511	$33,081	$49,631		$107,223
		Travel					
		Per diem					
	Training	Occupational Safety and Health Administration (OSHA)					
		Procedures					
	Maintenance	Concrete drill					
	Consumables	DROPEX^{Plus} & EXPRAY^{TM} kits		$832			$832
		Laboratory supplies, personal protective equipment (PPE), misc.		$6,750	$4,766	$	$11,516
		Fuel					
		Tools					
		Other (specified):					
	Residual waste handling	N/A					
	Off-site disposal	Hazardous waste					
	Analytical laboratory costs	NG – Method 8330/8332				$12,000	$12,000
		NC – MCAWW 353.2				$8,160	$8,160
		Shipping costs				$300	$300
		Data validation				$2,370	$2,370
	Long term monitoring	N/A					
Indirect costs	Equipment repair	Other (specified)					
Demobilization	Housekeeping	Site cleanup/maintenance					
		Personnel travel from site					
		Equipment travel from site					
		Shipping costs					
		Total	$37,229	$61,808	$54,397	$22,830	$176,264

Table 9. Demonstration Field Sampling Costs.

Cost Category	Subcategory	Details	Apportioned Costs for Field Sampling Activities	Total Estimated Demonstration Costs (Includes Shaw Costs) for On-Site Field Sampling
Start-up costs	Site characterization	N/A		
	Mobilization	Project planning	$5,000	$5,000
		Project coordination		
		Personnel travel to site	$5,845	$5,845
		Equipment travel to site		
		Shipping costs	$483	$483
Capital costs	Capital equipment purchase	N/A		
	Ancillary equipment purchase	N/A		
	Modifications	Concrete drill	$940	$940
	Structures installation	N/A		
	Engineering	N/A		
Operating costs	Capital equipment rental	Shaw Rental – laboratory trailer, misc		
	Ancillary equipment rental	Trailer generator and fuel		
		Phone services	$450	$450
	Supervision	Salary		
		Travel		
		Per diem		
	Operator laboratory	Salary	$24,511	$24,511
		Travel		
		Per diem		
	Training	OSHA		
		Procedures		
	Maintenance	Concrete drill		
	Consumables	DROPEX^{Plus} & EXPRAY^{TM} kits		
		Laboratory supplies, PPE, misc.		
		Fuel		
		Tools		
		Other (specified):		
	Residual waste handling	N/A		
	Off-site disposal	Hazardous waste		
	Analytical laboratory costs	NG – Method 8330/8332		
		NC – MCAWW 353.2		
		Shipping costs		
		Data validation		
	Long term monitoring	N/A		
Indirect costs	Equipment repair	Other (specified)		
Demobilization	Housekeeping	Site cleanup/maintenance		
		Personnel travel from site		
		Equipment travel from site		
		Shipping costs		
		Total	$37,229	$37,229
		NUMBER OF SAMPLE LOCATIONS		103
		UNIT COST PER SAMPLE LOCATION		$361

Table 10. Costs for On-Site Field Methods.

Cost Category	Sub Category	Details	Apportioned Costs for On-Site DROPEX^{Plus}/ EXPRAY^{TM}Analysis	Apportioned Costs for On-Site GC/TID Analysis	Apportioned Costs for On-Site Modified CRREL Analysis	Estimated Costs for On-Site Field Method Analysis
Start-up costs	Site characterization	N/A				
	Mobilization	Project planning	$2,500	$2,500	$2,500	$7,500
		Project coordination				
		Personnel travel to site	$3,333	$3,333	$3,334	$10,000
		Equipment travel to site				
		Shipping costs		$400	$400	$800
Capital costs	Capital equipment purchase	N/A				
	Ancillary equipment purchase	N/A				
	Modifications	Concrete drill				
	Structures installation	N/A				
	Engineering	N/A				
Operating costs	Capital equipment rental	Shaw Rental–Laboratory trailer, misc.	$402	$403	$403	$1,208
	Ancillary equipment rental	Trailer generator and fuel	$380	$380	$381	$1,141
		Phone services	$96	$200	$200	$496
	Supervision	Salary				
		Travel				
		Per diem				
	Operator laboratory	Salary	$2,200	$14,362	$16,519	$33,081
		Travel				
		Per diem				
	Training	OSHA				
		Procedures				
	Maintenance	Concrete drill				
	Consumables	DROPEX^{Plus} & EXPRAY^{TM} kits	$832			$832
		Laboratory supplies, PPE, misc.	$750	$2,500	$3,500	$6,750
		Fuel				
		Tools				
		Other (specified):				
	Residual waste handling	N/A				
	Off-site disposal	Hazardous waste				
	Analytical laboratory costs	NG – Method 8330/8332				
		NC – MCAWW 353.2				
		Shipping costs				
		Data validation				
	Long term monitoring	N/A				
Indirect costs	Equipment repair	Other (specified)				
Demobilization	Housekeeping	Site cleanup/maintenance				
		Personnel travel from site				
		Equipment travel from site				
		Shipping costs				
		Total	$10,493	$24,078	$27,237	$61,808
		NUMBER OF SAMPLES	151	115	115	115 – 151
		UNIT COST PER SAMPLE	$69	$209	$237	$516

Table 11. Demonstration Costs for Off-Site Reference Method Analyses for NC and NG.

Cost Category	Subcategory	Details	Apportioned Indirect Costs Associated with Off-Site STL Analyses	Off-Site STL Reference Method Analyses	Total Estimated Demonstration Costs (Includes Shaw Costs) for Off-Site Analyses
Start-up costs	Site characterization	N/A			
	Mobilization	Project planning			
		Project coordination			
		Personnel travel to site			
		Equipment travel to site			
		Shipping costs			
Capital costs	Capital equipment purchase	N/A			
	Ancillary equipment purchase	N/A			
	Modifications	Concrete drill			
	Structures installation	N/A			
	Engineering	N/A			
Operating costs	Capital equipment rental	Shaw Rental – Laboratory trailer, misc.			
	Ancillary equipment rental	Trailer generator and fuel			
		Phone services			
	Supervision	Salary			
		Travel			
		Per diem			
	Operator laboratory	Salary			
		Travel			
		Per diem			
	Training	OSHA			
		Procedures			
	Maintenance	Concrete drill			
	Consumables	DROPEX^{Plus} & EXPRAY^{TM} kits			
		Laboratory supplies, PPE, misc.			
		Fuel			
		Tools			
		Other (specified):			
	Residual waste handling	N/A			
	Off-site disposal	Hazardous waste			
	Analytical laboratory costs	NG – Method 8330/8332		$12,000	$12,000
		NC – MCAWW 353.2		$8,160	$8,160
		Shipping costs	$300		$300
		Data validation	$2,370		$2,370
	Long term monitoring	N/A			
Indirect costs	Equipment repair	Other (specified)			
Demobilization	Housekeeping	Site cleanup/maintenance			
		Personnel travel from site			
		Equipment travel from site			
		Shipping costs			
Administrative	Project management	Project management			
		Other Administrative costs			
	Reporting	Reports			
		Total	$2,670	$20,160	$22,830
				NUMBER OF SAMPLES	115
				UNIT COST PER SAMPLE	$199
				SAMPLE PREPARATION COSTS INCLUDED IN ON-SITE ANALYSIS COSTS	$4,960
				UNIT COST PER SAMPLE INCLUDING SAMPLE PREPARATION	$242

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6.0 IMPLEMENTATION ISSUES

6.1 COST OBSERVATIONS

Sampling costs were affected by cold temperatures and safety concerns related to obtaining samples below slabs that may contain residuals of explosives in quantities that would present a hazard. The cold outdoor temperatures necessitated special efforts to thaw soil for sampling beneath the concrete slab at concrete core sampling sites. A water-cooled, diamond tipped, hollow coring bit was used to drill through concrete floor slabs. This was chosen as a method to provide safe access to subslab samples. This method was expensive and likely caused some disturbance to the sample due to the water used to cool the drill bit. Alternative methods of obtaining these samples should continue to be investigated. Costs related to concrete cutting will also be affected by the thickness and strength of the concrete slab.

Off-site analytical costs per unit basis may be higher than what was experienced with the field demonstration. If rapid turnaround of analysis results is required to support on-site operations, then an off-site laboratory would typically charge a surcharge of 50% to 100% of the normal turnaround analytical price for 24- to 48-hour turnaround of results.

Off-site analyses may also incur additional costs associated with sample preparation, which was performed on-site for the demonstration samples that were sent to the off-site laboratory. Sample preparation included sample drying, particle size reduction and homogenization. This cost would most likely be in the form of on-site labor or additional costs charged by the off-site laboratory if they were willing to perform the necessary sample preparation.

On-site analytical costs for the field methods are expected to be lower than what were experienced in the field demonstration. The field demonstration included method evaluation and development, so the experience level and associated pay rate for analysts were higher than what is needed for field work using established analytical procedures. The most expensive pieces of equipment required for on-site analyses are the portable field GC/TID at a cost of approximately $10,000 and a portable field spectrophotometer at a cost of approximately $2,000. On-site analyses would also require laboratory type facilities and equipment including a fume hood, balance, blender, shaker table, oven, solvents, associated glassware and supplies, etc.

6.2 PERFORMANCE OBSERVATIONS

6.2.1 EXPRAY^{TM} and DROPEX^{Plus} Test Kits for NC and NG

Overall EXPRAY^{TM} and DROPEX^{Plus} are thought to be useful tools in the field for screening the presence of NC and or NG in sample extracts at above detection levels. Detection levels are matrix and analyte dependent, ranging from 40 mg/kg for NG on soil extracts to 2,500 mg/kg for NC on wood extracts, with low confidence in results at or near the detection limit. The field method should be used as a screening tool only in combination with other supportive methods of analysis.

The EXPRAY™ test, while slightly less sensitive, is easier to evaluate as either detect or non-detect. DROPEX^{Plus} when applied seems to spread out more and have more prevalent yellow discoloration, which tends to compromise detection of the pink color.

Both of the field kits are easy to use with little specialized training and equipment.

6.2.2 CRREL Methodology for NG/NC

The CRREL RDX method of analysis gives a relatively low response for NC compared to NG, and the NC response is easily impacted by matrix interferences. The wood matrix interferes with the method such that calibration with wood matrix standards is not possible due to extremely low and nonreproducible response. Modifications to the CRREL RDX procedure were made to greatly increase the method response for NC while retaining the response for NG. The modified CRREL method that was developed appears to perform well for NC and NG analysis. It provides low detection limits in the range of 2 mg/kg to 10 mg/kg and predictable analyte response for the matrices used in this test. Neither CRREL method is specific to NG or NC and both provide a response to the total of NG and NC. The modified CRREL method, however, produces a similar response for each analyte such that the total analytical result can be expressed nearly equivalently as NG, NC, or a mixture of NG and NC within 75% to 130% accuracy.

The analysis of NC and NG on concrete is hampered by decomposition of the explosive compounds due to the alkaline nature of the concrete matrix, which causes alkaline hydrolysis of the compound nitro groups. The instability of NC/NG compounds on concrete matrix makes analysis difficult because of the dynamic impact on sample concentrations, and the effect on matrix standards.

CRREL results are biased low in comparison to the STL reference method results, but STL Method 353.2 results are believed to be biased high due to matrix interference or contamination phenomenon that was observed on method blanks and clean background matrix analyses.

Nonhomogeneous sample material and sources of contamination, such as pieces of propellant material, make preparing a homogeneous sample difficult for reproducible results or split sample result comparison.

One field chemist with experience in wet chemistry techniques is required for on-site analysis by the CRREL methods.

6.2.3 GC/TID Method for NG

GC/TID analysis of NG is selective and sensitive with detection limits in the range of 2 mg/kg to 5 mg/kg, which is comparable to the reference method. In general, reliability of the GC/TID ability to detect NG on the building materials is consistent with the reference Method 8330. Both methods may be subject to matrix interference effects and QC samples should be included to help assess data quality.

One field chemist with experience in GC is required for onsite analysis by GC/TID.

Maintaining instrument sensitivity requires frequent cutting of the injection end of the column. The frequency is matrix-dependent and thought to be due to loading or degradation of the column material by nontarget constituents in the sample extract. This problem was most prevalent with the wood samples.

6.3 SCALE-UP

The performance issues discussed above are applicable to use of the technologies on larger scale projects.

6.4 LESSONS LEARNED

6.4.1 EXPRAY^{TM}/DROPEX^{Plus}—Detection Limits

EXPRAY^{TM} and DROPEX^{Plus} tests have limited detection limits for NC and NG that are matrix dependent. They are most useful as a screening tool for identifying areas of significant explosives contamination that are on the order of 50 mg/kg to 2,500 mg/kg (0.25%), depending on the matrix, and above. For comparison with NC and NG reference methods for evaluation in future studies, it would be more beneficial if a significant number of sample concentrations were more in the range of detection for these tests, i.e., greater than 100 mg/kg.

6.4.2 Sample Homogeneity

There was considerable scatter in the RPD between results from the reference and field methods as well as duplicate sample analyses by the same method, and it is believed that a large part of this was due to nonhomogeneity of the samples. Contamination of building materials (concrete and wood) was likely concentrated on exposed surfaces of the material. Chopping or crushing the sample to reduce the matrix particle size to about ¼ inch was possibly not small enough to provide sufficient distribution of contaminated surface pieces for uniform sampling. In addition, soil samples contained pieces of propellant material that made preparing a homogeneous sample difficult. In future evaluations, more effort should be put into assuring more homogeneity in the bulk sample either by additional size reduction of sample particles or by use of a larger sample aliquot for analysis (extraction) or perhaps by analyzing splits of sample extracts.

6.4.3 CRREL RDX Method—Low Response for NC

The CRREL RDX method of analysis gave a relatively low response for NC compared to NG that was easily impacted by matrix interferences. Modifications that were made to the CRREL RDX procedure greatly increased the method response for NC and retained the response for NG. The use of the modified CRREL method is recommended for analysis of NG, NC, or mixtures of NG and NC in future work.

6.4.4 Effect of Concrete Matrix on NC and NG

NC and NG are not stable on the concrete material matrix. Due to the alkaline nature of the matrix, the compounds are believed to be degraded by alkaline hydrolysis of the compound nitro groups. Calibration of the method using matrix standards should be performed by adding standard reference compounds to matrix extracts rather than spiking directly onto the matrix

where degradation can readily occur. Because of the instability of the compounds on the matrix, concrete samples should not be used in the method evaluation. Too few positive responses are obtained and the matrix effect during the sample analysis process cannot be predicted.

6.4.5 Reference Method of Analysis for NC

Because of the poor performance for the MCAWW 353.2 method for analysis of NC concentrations, especially below 80 mg/kg, that was noted in the bench-scale study, a practical quantitation limit higher than the laboratory reporting limit of 2 mg/kg should be considered for application to sample analysis results. Alternatively, a different reference method other than the STL modified MCAWW 353.2 should be researched for use in comparison to the Modified CRREL method.

6.4.6 Reference Method Data Quality

The data quality from the reference methods was not sufficiently defined in the field demonstration testing by the laboratory batch QC samples. There was contamination in some of the method blank sample analyses for NC, and there were some problems with matrix spike samples for both analytes that were either not determined due to dilution of the sample or analyte recoveries that were outside QC requirements. Some clean matrix blank samples and field spiked matrix samples should be submitted along with the field samples to better define the data quality from the reference method analyses.

6.4.7 GC/TID Performance Degradation

Maintaining instrument sensitivity for NG required frequent cutting of the injection end of the column. The frequency is matrix-dependent and thought to be due to loading or degradation of the column material by nontarget constituents in the sample. This problem was most prevalent with the wood samples. Check standards should be analyzed frequently—every 5 to 10 samples—to monitor system performance.

6.5 APPROACH TO REGULATORY COMPLIANCE AND ACCEPTANCE

The WDNR (the lead regulatory agency at BAAAP) approved the Demonstration Plan (Shaw, 2004) and has expressed considerable interest in characterizing the buildings at BAAAP so that they may be safely transferred out of DoD control. Many other regulatory agencies find themselves in the position of desiring defendable characterization for DoD buildings so that land transfer decisions can be made safely and effectively. Acceptance of the technologies by the WDNR or other agencies is unlikely at this time due to the following:

- Limited information for soil and concrete analysis due to the small number of samples obtained with sufficient NG concentration for meaningful evaluation
- Information obtained is affected by results from analysis of nonhomogeneous samples
- Information obtained is affected by results from analysis by reference methods with undefined data quality.

For these reasons it is believed that further testing is necessary to gain regulatory acceptance of the approaches used.

Recommended additional testing to validate methods includes the following:

- EXPRAY™ and DROPEX^{Plus} tests are needed using a significant number of sample concentrations more in the range of detection for these tests, i.e., greater than 100 mg/kg.
- Tests to validate methodologies for concrete matrix need to incorporate analyses performed on background concrete sample extracts that are spiked with known NG and NC concentrations. At a minimum, standards prepared in this manner should be used to calibrate the GC/TID and modified CRREL methods. This would remove the complication of working with dynamic concentrations due to matrix degradation of the NG and NC analytes and provide simulated sample extracts at meaningful concentrations for method validation. Spiked extracts can then be split for analysis by EXPRAY™ and DROPEX^{Plus}, GC/TID, modified CRREL, and possibly the reference analysis methods as well.
- Analysis of site samples by any of the technologies on any of the matrices should be performed on well-homogenized matrix samples with particle sizes smaller than what was used in this study, which was approximately ¼ inch. Particle sizes for soil and concrete should be reduced to less than about 1 mm diameter before homogenization and aliquoting for sample splits. Wood sample particles should be reduced to less than about 3 mm.
- Soil and wood sample analyses by the outside analytical reference laboratory should be performed on sample splits using both well-homogenized matrix and some extracts of the matrix to separate the nonhomogeneity factor from split analyses and evaluate its impact if this can be arranged with the outside reference laboratory.
- Sample analyses by the technologies should also incorporate a program of blind blank (clean matrix), blind matrix spike, and blind matrix extract spike samples to define the quality of the data obtained by each of the methods to be used in the evaluation. This should include the reference method analyses as well. Spiking of the samples would also assure there are a sufficient number of positive results in the desired concentration range for method evaluation.
- Tests using the CRREL technology should be performed using the method modification developed in this work as the original CRREL RDX method is not suitable for analysis of NC or mixtures of NC and NG.

This testing can be performed in a program that is similar to the bench-scale and field demonstration tests. Some of the samples previously collected may be used as they are still retained at the laboratory and many have sufficient sample for re-analysis. These samples may be supplemented by additional samples from known contaminated or highly suspected contaminated locations at BAAAP. It is felt that on-site method testing is not necessary, since

the ability to perform the technologies on-site was demonstrated in the field demonstration study. An analysis program could be carefully designed incorporating the recommendations above. Test method analyses would be performed in the laboratory and split samples would be sent for outside laboratory analysis using the reference methods.

The testing program should incorporate 20-30 samples of each matrix using reduced particle size and well-homogenized samples. Splits of the matrix samples will be analyzed by the study technologies and sent for reference analysis along with selected extract splits for each matrix (if acceptable to the outside reference laboratory). Blank (clean matrix), blind matrix spike, and blind matrix extract spike samples would also be incorporated.

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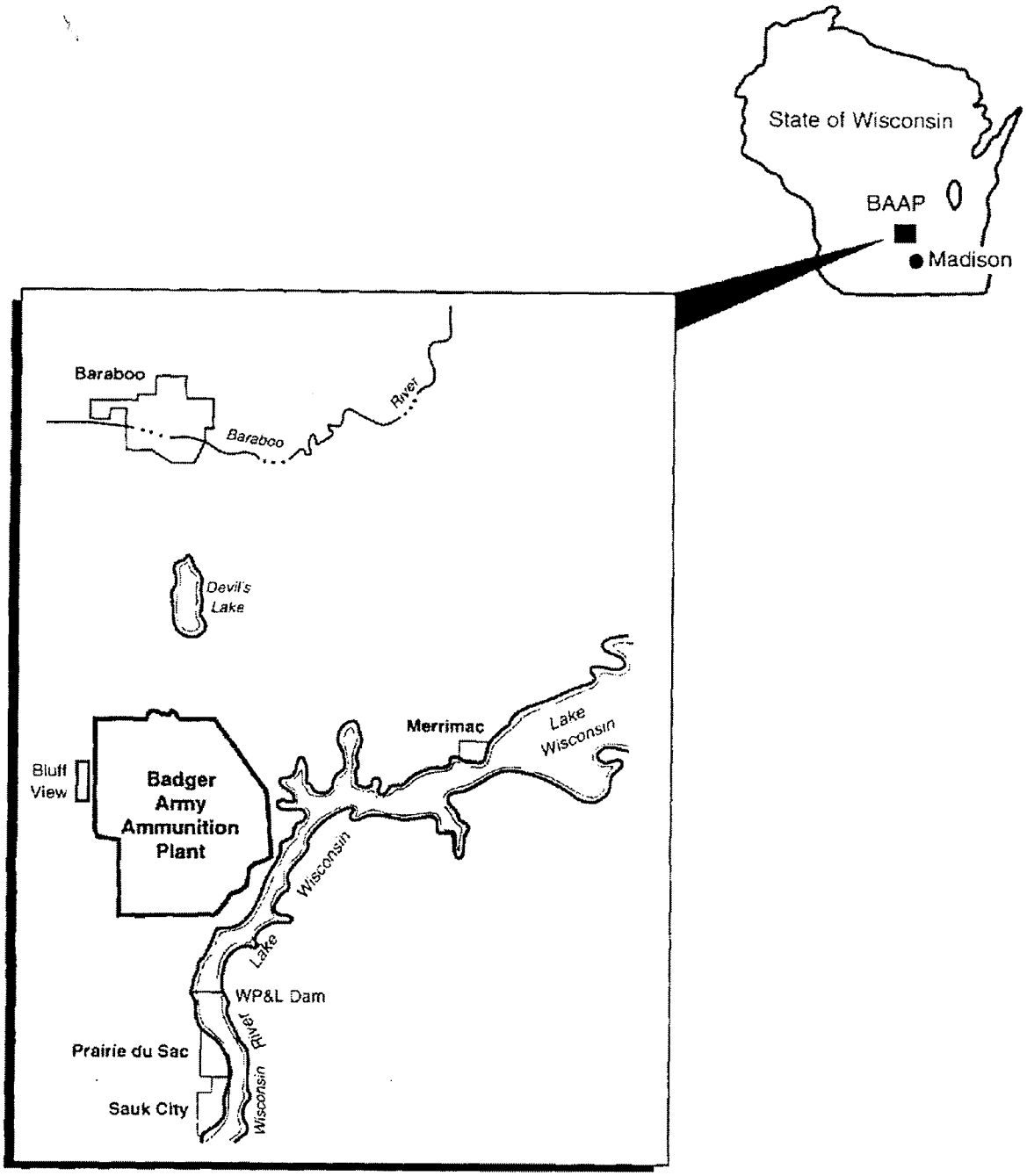
APPENDIX A

POINTS OF CONTACT

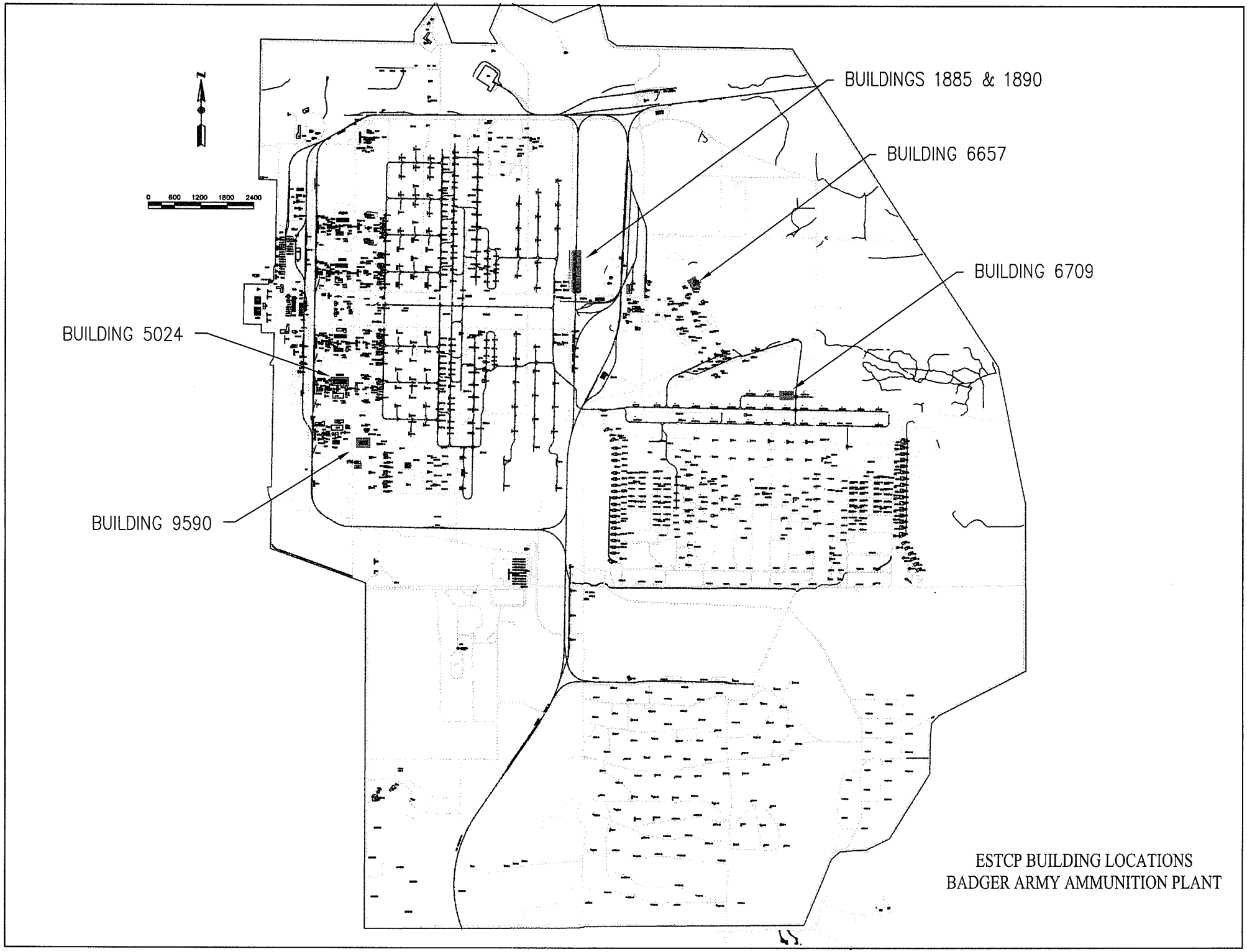
Point of Contact	Organization	Phone/Fax/E-Mail	Role
Jay Hodges	USACE 106 South 15th Street Omaha, NE 68102	Phone: 402-221-3986 Fax: 402-221-7838 E-mail: jay.d.hodges@usace.army.mil	USACE Project Manager/Principal Investigator
Kathleen Romalia	Shaw Environmental, Inc. 9201 East Dry Creek Road Centennial, CO 80112	Phone: 303-741-7131 Fax: 303-741-7322 E-mail: kathleen.romalia@shawgrp.com	Shaw Environmental, Inc. Project Manager
Joan Kenney	U.S. Army Badger Army Ammunition Plant 2 Badger Road Baraboo, WI 53913	Phone: 608-643-0073 Fax: 608-643-3364 E-mail: joan.m.kenney@us.army.mil	Installation Director
Frank Anstett	SpecPro Badger Army Ammunition Plant 1 Badger Road Baraboo, WI 53913	Phone: 608-643-5302 Fax: 608-643-2674 E-mail: fanstett@spec-pro.com	SpecPro, Program Manager
Duane Root	Shaw Environmental & Infrastructure, Inc. 304 Directors Drive Knoxville, TN 37923	Phone: 865-694-7360 Fax: 865-694-9573 E-mail: duane.root@shawgrp.com	Principal Scientist for Laboratory Testing
Ellen Lay	Shaw Environmental & Infrastructure, Inc. 304 Directors Drive Knoxville, TN 37923	Phone: 865-560-5263 Fax: 865-694-9573 E-mail: ellen.lay@shawgrp.com	Laboratory Project Chemist for CRREL Methodology
Ed Morren	Shaw Environmental & Infrastructure, Inc. 304 Directors Drive Knoxville, TN 37923	Phone: 865-694-7309 Fax: 865-694-9573 E-mail: stephen.crouch@shawgrp.com	Laboratory Project Chemist – EXPRAY™ / DROPEX^{Plus} and Field Sampling
Stephen Crouch	Shaw Environmental & Infrastructure, Inc. 304 Directors Drive Knoxville, TN 37923	Phone: 865-560-5267 Fax: 865-694-9573 E-mail: stephen.crouch@shawgrp.com	Laboratory Project Chemist for GC/TID Method
Hank Kuehling	Wisconsin Department of Natural Resources 3911 Fish Hatchery Road Fitchburg, WI 53711	Phone: 608-275-3310 Fax: 608-275-3338 E-mail: kuehlingh@dnr.state.wi.us	District Hydrogeologist

APPENDIX B

MAPS



BADGER ARMY AMMUNITION PLANT
SITE LOCATION



ESTCP BUILDING LOCATIONS
BADGER ARMY AMMUNITION PLANT

APPENDIX C

BENCH-SCALE STUDY REPORT

Environmental Security Technology Certification Program

Bench-Scale Study Report
Verification of Field Test Methods for Nitrocellulose- and Nitroglycerine-Spiked Samples of Soil and Building Materials

Badger Army Ammunition Plant
Baraboo, Wisconsin

March 31, 2006

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LIST OF ACRONYMS

BAAAP	Badger Army Ammunition Plant
°C	degrees Celsius
cm	centimeter
CRREL	Cold Regions Research and Engineering Laboratory
EPA	U.S. Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
GC	gas chromatography
HPLC	high-performance liquid chromatography
MCAWW	Methods for the Chemical Analysis of Wastewater
mg/kg	milligrams per kilogram
mg/L	milligrams per liter
µL	microliter
mL	milliliter
mm	millimeter
NC	nitrocellulose
NG	nitroglycerine
Nm	nanometer
psi	pounds per square inch
RDX	cyclotrimethylenetrinitramine
SRI	SRI Instruments
STL	Severn Trent Laboratories
TAL	Technology Applications Laboratory
TID	thermionic ionization detector

BENCH-SCALE STUDY REPORT
VERIFICATION OF FIELD TEST METHODS FOR NITROCELLULOSE- AND NITROGLYCERINE-SPIKED SAMPLES OF SOIL AND BUILDING MATERIALS
BADGER ARMY AMMUNITION PLANT
BARABOO, WISCONSIN

1.0 INTRODUCTION

1.1 Background

This report describes bench-scale studies performed by the Shaw Environmental, Inc. (Shaw) Technology Applications Laboratory (TAL) in Knoxville, Tennessee, on soil and building material samples collected from the Badger Army Ammunition Plant (BAAAP) site in Baraboo, Wisconsin. The activities described were performed by Shaw Environmental, Inc. (Shaw) as the prime contractor to the U.S. Army Corps of Engineers Omaha District (USACE) for the U.S. Department of Defense Environmental Security Technology Certification Program (ESTCP). The bench scale testing was conducted to assess the performance of four on-site technologies for nitroglycerine (NG) and nitrocellulose (NC) detection that are expected to be used during a field demonstration at the BAAAP site in Baraboo, WI. The methods evaluated on NC/NG spiked materials included Raman spectroscopy, EXPRAY™/ DROPEX^{PLUS} colorimetric indicator, gas chromatography (GC)/thermionic ionization detector (TID), and the Cold Regions Research and Engineering Laboratory (CRREL) Royal Demolition Explosive (RDX) colorimetric method.

1.2 Study Objectives

The purpose of the bench-scale study was to verify field technologies for NC and NG detection in building materials and soil prior to their implementation in the field demonstration. The technology verification will result in building characterization procedures that may benefit many U.S. Army ammunition plants with similar explosive materials. The implementation of these procedures may result in substantial savings over conventional remedial investigation techniques of explosive-contaminated buildings. The objectives of the study are as follows:

- Obtain usable calibration data for NC detection using the quantitative CRREL screening method for RDX (Walsh and Jenkins, 1991 and EPA, 2000) and the Methods for the Chemical Analysis of Water and Wastes (MCAWW) 353.2 method for NC (EPA, 1983) using samples spiked with NC material similar to the form found at BAAAP.

- Evaluate the repeatability of qualitative NC detection results of the EXPRAY™™ and Raman screening methods and quantitative testing using MCAWW 353.2 for NC (i.e., determine the likelihood of false positive or false negative results from the screening methods versus the quantitative analytical results).

- Evaluate the repeatability of qualitative NG detection results between the EXPRAY™™ and Raman screening methods and quantitative testing using U.S. Environmental Protection Agency (EPA) SW-846 Method 8332 (EPA, 1998)/Method 8330 (EPA, 1995) and gas chromatography (GC)/thermionic ionization detector (TID) for NG (Hewitt, 2002), i.e., determine the likelihood of false positive or false negative results from the screening methods versus the quantitative analytical results.

- Evaluate the repeatability of quantitative analytical results between the ESTCP demonstration methods for NC detection (CRREL RDX method and the MCAWW 353.2 method).

- Evaluate the repeatability of the quantitative analytical results between the ESTCP demonstration methods for NG detection (CRREL RDX method, EPA SW-846 Method 8332/8330, and GC/TID. GC/TID was not used in the previous ESTCP demonstration (Stone & Webster, 2003), but has been used for field detection of NG in other investigations.

- Determine the effect of mixtures of NC and NG in the same sample on the usability of quantitative results obtained from the CRREL RDX method, which is nonspecific for NC or NG; the MCAWW 353.2 method, which is specific for NC; and GC/TID which is specific for NG.

2.0 TESTING DESIGN AND DESCRIPTION

A bench-scale study for NG and NC in soil and building materials was performed to verify the usability of the work flow in a technology demonstration for field characterization of buildings used in the production of NC and NG. The specific goals of the study are (1) verify that usable calibration data may be obtained for BAAAP NC analysis using the CRREL RDX method and the MCAWW 353.2 method, (2) compare the qualitative screening indications from EXPRAY™™/ DROPEX^{PLUS} and Raman screening methods to the quantitative results for NC analysis using the MCAWW 353.2 method for NC, (3) compare the qualitative screening indications from EXPRAY™™ and Raman screening with the quantitative analytical results for NG using EPA SW-846 Method 8332 and GC/TID; (4) compare the quantitative analytical results between the ESTCP demonstration methods for NG detection (CRREL RDX method, EPA SW-846 Method 8330/8332, and GC/TID), (5) compare the quantitative results between the demonstration methods for NC (CRREL RDX method and the MCAWW 353.2 method), and (6) determine the effect of NC and NG mixtures in the same sample on the quantitative results obtained from the nonspecific methods and compound-specific methods.

Specific tasks required to complete this study were as follows:

- Collection and analysis of background samples of soil, concrete, wood, and wallboard from BAAAP buildings not used in explosive production
- Preparation of spiked samples with known amounts of NC and/or NG and blanks
- Screening spiked samples for NC and/or NG using EXPRAY™™/ DROPEX^{PLUS} and Raman spectroscopy (qualitative analyses)
- Quantitative analysis for NC+NG using the CRREL RDX method and verification of the calibration curve obtained
- Quantitative analysis for NC using the MCAWW 353.2 method and verification of the calibration curve obtained
- Quantitative analysis for NG using GC/TID
- Quantitative analysis for NG using EPA SW-846 Method 8330/8332
- Comparison of the results between screening/analysis for NC
- Comparison of the results between screening/analysis for NG
- Analysis of spiked samples containing both NC and NG using the CRREL RDX method, the MCAWW 353.2 method, GC/TID, and EPA SW-846 Method 8330/8332 and comparison of results.

Each of the above tasks is described in the following sections.

2.1 Sample Collection and Homogenization

At the time of converting the BAAAP facility to standby status, buildings at BAAAP were classified by their assessed level of contamination. A recent survey of the buildings was conducted by the Army to verify these classifications. Some buildings are known to have never been used for explosive material production and others were assigned designations based on the possible level of exposure to these materials. Many of the plant buildings were constructed of the same materials.

Uncontaminated samples of soil and building materials were collected using the building survey (Plexus Scientific, 2004) to determine structures not used in explosives manufacturing. The materials were examined for similarity to the materials used in production buildings, and bulk samples of soil, concrete, wood framing, and wallboard were collected and sent to the Shaw TAL in Knoxville, Tennessee. Test samples were received on May 31, 2005 (wood, soil, and concrete) and June 2, 2005 (wallboard). An additional wood sample was collected from the site for comparison purposes. A clean 2-by-4-inch plank was also obtained from Home Depot on June 21, 2005 for additional background testing of uncontaminated wood. The site materials and the Home Depot wood sample were each assigned a lab identification number upon receipt and described as follows:

Date	Material	Sample Wt (pounds)	Sample Description	Sample ID#
5/31/05	WD-Site Wood	15.5	2-by- 4-inch planks	7850
5/31/05	SS-Site Soil	23.0	two 1-gallon bags	7851
5/31/05	CM-Concrete	21.0	Large chunks	7852
6/2/05	WB-Wallboard	15.0	¼-by-1-foot sections	7857
6/21/05	WD2-Site Wood	15.0	2-by-4-inch planks	7850WD(2)
6/21/05	HD-Wood	15.0	2-by-4-inch planks	HD-000

The bulk sample of each matrix was reduced by hand or mechanical means to pass a #4 sieve and mixed until visually uniform in appearance. Wood chips/sawdust were obtained using a planning saw and a 3/8-inch drill bit. The site soil was mixed by hand in a stainless-steel mixing bowl until visually homogenous. Concrete was placed on heavy plastic and crushed into small pieces using a 2-pound steel hammer. The wallboard, an asbestos-containing material, was placed into very heavy plastic bags, covered with duct tape, and broken into small pieces using a 2-pound steel hammer. The broken pieces were then further reduced in a hand grinder. The wallboard samples were handled contained in plastic baggies and inside a hood equipped with a high-efficiency particulate air filter. Sufficient site material was processed to obtain three to four kilograms of each material type to be tested. Each sample composite was divided into two separate samples (A and B) and stored in a ziplock bag pending spike addition and further testing. Two representative aliquots (A and B) of each test matrix were placed into 4-ounce amber bottles and submitted to Severn Trent Laboratories (STL) in Sacramento, California for baseline analysis by the MCAWW 353.2 method for nitrate/nitrite and NC and by EPA SW-846 Method 8330 for NG to verify that the matrices are uncontaminated and to establish background concentrations. Each sample matrix was also analyzed for percent solids. The baseline samples to be tested were identified as described in Table 2-1 and pictured on Figures 2-1 thru 2-4.

Table 2-1
BAAAP Bench-Scale Testing Baseline Data Summary

Sample ID	Units	% Solids	Method 8330 Nitroglycerine	Method 353.2 Nitrocellulose as N	Method 353.2 Nitrate-Nitrite
BS-BL-SS-A000	mg/kg	96.3	ND<0.5	2.3	1.3
BS-BL-SS-B000	mg/kg		ND<0.5	2.2	1.4
BS-BL-CM-A000	mg/kg	96.8	ND<0.5	2.3	0.91
BS-BL-CM-B000	mg/kg		ND<0.5	2.2	0.90
BS-BL-WD-A000	mg/kg	90.1	ND<0.5	26.2	3.2
BS-BL-WD-B000	mg/kg		ND<0.5	25.4	3.2
BS-BL-WD-A000RR*	mg/kg		NA	9.3	3.5
BS-BL-WD2-A000	mg/kg		NA	18.9	8.6
BS-BL-HD-A001	mg/kg		NA	6.1	0.66
BS-BL-WB-A000	mg/kg	95.5	ND<0.5	15.5	24.1
BS-BL-WB-B000	mg/kg		ND<0.5	17.1	25.1

BS – Benchscale; BL – Baseline
SS - site soil; CM - concrete; WD - wood; WB - Wallboard; WD2 - 2nd BAAAP site wood HD - Home Depot plank
A, B - sample splits; RR - Rerun

*The original wood sample received on May 31, 2005 contained the lowest background levels of nitrite/nitrate and was selected for the benchscale testing.

ND – Nondetect.
NA – Not applicable.
mg/kg – milligrams per kilogram.

BAAAP Site Composite Material

Figure 2-1. Soil Composite

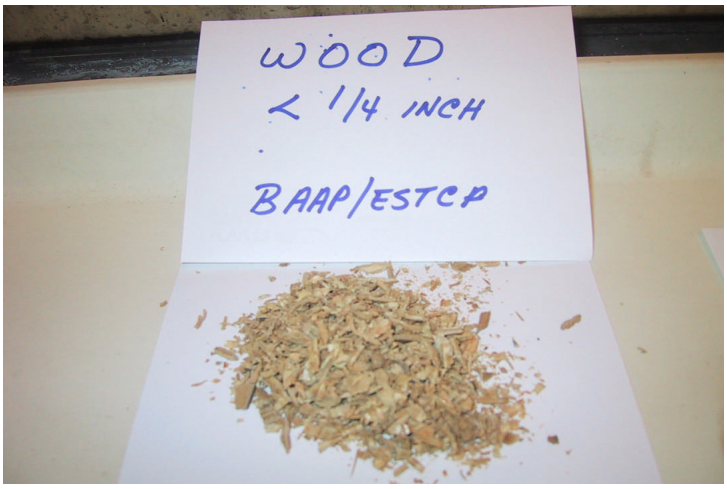


Figure 2-2. Wood Composite

Figure 2-3. Wallboard Composite

Figure 2-4. Concrete Composite

2.2 Sample Spiking Scheme

After outside lab confirmation that the four matrices contained acceptable background levels, sample aliquots of each matrix were weighed out in triplicate for each of three sample study groups: one group of 3 x 14 aliquots of 20 grams each for NC spiked samples, one group of 3 x 12 aliquots of 20 grams each for NG spiked samples, and a group of 3 x 6 aliquots of 20 grams each for NC/NG combined spiked samples. Sample aliquots of soil, wallboard and concrete were weighed into amber 4-ounce wide-mouth jars and labeled for spiking. Wood samples were weighed into 8-ounce jars due to the bulk size of the wood and to allow for mixing. The triplicate samples were handled as follows; one was submitted to STL for analysis by the respective reference method(s), one was extracted for analysis by the CRREL method at the TDL, and one was extracted for GC/TID, Raman, and DropEx/EXPRAY™ analyses at the TDL.

The first group, 3 x 14 aliquots of 20 grams of each matrix, was spiked using a slurry of NC solid material prepared from nitrocellulose suspended in nitrate/nitrite-free water. The spike solutions were prepared from nitrocellulose reference material in stock at the TAL (71 percent flake with isopropyl alcohol, RS ½ sec, lot 9H-9027, Hercules, Inc.) based on the procedure described in Appendix A. A blender and sonication were used to reduce the particle size to provide a uniform spiking material. A stock solution of 1.5 percent (by dry weight) nitrocellulose was initially prepared by sonication in nitrate/nitrite-free water and then diluted to obtain 2,000 (mg/L) and 200 mg/L solutions. Spike solutions were stirred constantly to keep particles in uniform suspension while in use.

The second group consisting of 3 x 12 aliquots of 20 grams of each matrix was spiked using a commercially prepared stock solution of 10 milligrams per milliliter NG in methanol obtained from Accutest Labs. A 10x dilution of the stock solution was made in acetone to make a 1,000 mg/L stock solution for lower spike concentrations.

The material spike concentrations for these samples were used as described in the work plan and are based on anticipated method capabilities. NC spike concentrations ranged from 0 to 40,000 milligrams per kilogram (mg/kg) and NG spike concentrations from 0 to 400 mg/kg.

Of the first group (NC group) eight of the samples for each matrix were used for developing a calibration curve for the analytical equipment. Calibration sample spike concentrations were 0, 5, 20, 50, 100, 400, 4,000, and 40,000 mg/kg NC. Six test samples for each matrix were used for verification samples and spiked at 0, 2.5, 10, 80, 250, and 2,500 mg/kg NC, respectively. A similar suite of samples was used for the second group (NG group) of samples, except the first six samples were used to obtain calibration data spiked at 0, 5, 20, 50, 100, and 400 mg/kg. The remaining six test samples were verification samples at spike concentrations of 0, 2.5, 10, 40, 80, and 250 mg/kg NG.

The third group of samples was used for spiking combinations of NC and NG. These samples were prepared after the results of the analyses of the first two groups were evaluated in order to optimize test conditions and to obtain value-added data in the combined spike samples

The third group of samples was used for analysis after being spiked with a combination of NC and NG. The mixture concentrations were established after the best working concentration ranges were determined from the calibration testing. Combined NC/NG spike samples ranged from 0 to 400 mg/kg NG and 0 to 4,000 mg/kg NC. Nitrocellulose was 6 to 8 times less sensitive in testing; therefore, spike concentrations for NC were a factor of 10 higher than these for NG. Spike levels for NG were established at 0, 5, 25, 100, and 400 mg/kg. NC was spiked at concentrations of 0, 50, 250, 1,000, and 4000 mg/kg, respectively. NG/NC was prepared in duplicate. An additional sample was also tested with NG at 400 mg/kg and NC at 250 mg/kg to evaluate any NC/NG ratio effects.

Matrix blanks were prepared as part of each sample suite. Each prepared sample was individually spiked and homogenized as much as possible by thorough mixing with a spatula. Nitrate-free water was added as needed for safety and to aid in dispersing the spike aliquot. The spiked samples were allowed to air dry in a hood overnight or until visually dry. Each dried spiked sample aliquot was mixed with a stainless-steel spatula until visually homogenous and submitted for required analysis.

Each of the three aliquots at each spike level for each test group was prepared for the appropriate analysis. One set of the 20-gram samples was packed into a cooler at 4 degrees Celsius (°C) and submitted to STL for quantitative analysis by accepted laboratory reference methods MCAWW 353.2 for NC and/or EPA SW-846 8330/8332 for NG.

Table 2-2 presents the sample preparation schemes for the testing groups described above.

Table 2-2
Summary of Sampling and Analysis Requirements – Bench-Scale Study

Analyte	Matrix	Analytical Method	Number of Calibration Samples	Calibration Concentrations NC (mg/kg)	Number of Test Samples	Test Sample Concentrations NC (mg/kg)	Total No. Samples
Nitrocellulose (NC)	Soil	CRREL RDX	7 + 1 Blank	0, 5, 20, 50, 100, 400, 4000, 40000	5 + 1 Blank	0, 2.5, 10, 80, 250, 2500	14
		EXPRAY™®/ DROPEX PLUS					
		Raman					
		MCAWW 353.2(1)	7 + 1 Blank	"	5 + 1 Blank	"	14
	Concrete	CRREL RDX	7 + 1 Blank	0, 5, 20, 50, 100, 400, 4000, 40000	5 + 1 Blank	0, 2.5, 10, 80, 250, 2500	14
		EXPRAY™/ DROPEX PLUS					
		Raman					
		MCAWW 353.2(1)	7 + 1 Blank	"	5 + 1 Blank	"	14
	Wallboard	CRREL RDX	7 + 1 Blank	0, 5, 20, 50, 100, 400, 4000, 40000	5 + 1 Blank	0, 2.5, 10, 80, 250, 2500	14
		EXPRAY™/ DROPEX PLUS					
		Raman					
		MCAWW 353.2(1)	7 + 1 Blank	"	5 + 1 Blank	"	14
	Wood	CRREL RDX	7 + 1 Blank	0, 5, 20, 50, 100, 400, 4000, 40000	5 + 1 Blank	0, 2.5, 10, 80, 250, 2500	14
		EXPRAY™/ DROPEX PLUS					
		Raman					
		MCAWW 353.2(1)	7 + 1 Blank	"	5 + 1 Blank	"	14

Notes: (1) Separate laboratory- STL, Sacramento, California.

Table 2-2. (continued)

Analyte	Matrix	Analytical Method	Number of Calibration Samples	Calibration Concentrations NG (mg/kg)	Number of Test Samples	Test Sample Concentrations NG (mg/kg)	Total No. Samples
Nitroglycerin (NG)	Soil	CRREL RDX	5 + 1 Blank	0, 5, 20, 50, 100, 400	5 + 1 Blank	0, 2.5, 10, 40, 80, 250	12
		EXPRAY™/ DROPEX^{PLUS}					
		Raman					
		GC/TID	5 + 1 Blank	"	5 + 1 Blank	"	12
		EPA Method 8332(1)	5 + 1 Blank	"	5 + 1 Blank	"	12
	Concrete	CRREL RDX	5 + 1 Blank	0, 5, 20, 50, 100, 400	5 + 1 Blank	0, 2.5, 10, 40, 80, 250	12
		EXPRAY™/ DROPEX^{PLUS}					
		Raman					
		GC/TID	5 + 1 Blank	"	5 + 1 Blank	"	12
		EPA Method 8332(1)	5 + 1 Blank	"	5 + 1 Blank	"	12
	Wallboard	CRREL RDX	5 + 1 Blank	0, 5, 20, 50, 100, 400	5 + 1 Blank	0, 2.5, 10, 40, 80, 250	12
		EXPRAY™/ DROPEX^{PLUS}					
		Raman					
		GC/TID	5 + 1 Blank	"	5 + 1 Blank	"	12
		EPA Method 8332(1)	5 + 1 Blank	"	5 + 1 Blank	"	12
	Wood	CRREL RDX	5 + 1 Blank	0, 5, 20, 50, 100, 400	5 + 1 Blank	0, 2.5, 10, 40, 80, 250	12
		EXPRAY™/ DROPEX^{PLUS}					
		Raman					
		GC/TID	5 + 1 Blank	"	5 + 1 Blank	"	12
		EPA Method 8332	5 + 1 Blank	"	5 + 1 Blank	"	12

Notes:
(1) Separate laboratory – STL, Sacramento, California.

Table 2-2. (continued)

Analyte	Matrix	Analytical Method	Number of Calibration Samples	Calibration Concentrations NC+NG (mg/kg)	Number of Test Samples	Test Sample Concentrations NC+NG (mg/kg)	Total No. Samples
NG + NC	Soil	CRREL RDX	0	N/A	6	0/0, 50/5, 250/25, 1000/100, 4000/400 250/400	6
		EXPRAY™/ DROPEX^{PLUS}					
		Raman					
		GC/TID	0	"	6	"	6
		EPA Method 8332(1)	0	"	6	"	6
		MCAWW 353.2(1)	0	"	6	"	6
	Concrete	CRREL RDX	0	N/A	6	0/0, 50/5, 250/25, 1000/100, 4000/400 250/400	6
		EXPRAY™/ DROPEX^{PLUS}					
		Raman					
		GC/TID	0	-	6	"	6
		EPA Method 8332(1)	0	-	6	"	6
		MCAWW 353.2(1)	0	"	6	"	6
	Wallboard	CRREL RDX	0	N/A	6	0/0, 50/5, 250/25, 1000/100, 4000/400 250/400	6
		EXPRAY™/ DROPEX^{PLUS}					
		Raman					
		GC/TID	0	-	6	"	6
		EPA Method 8332(1)	0	-	6	"	6
		MCAWW 353.2(1)	0	"	6	"	6
	Wood	CRREL RDX	0	N/A	6	0/0, 50/5, 250/25, 1000/100, 4000/400 250/400	6
		EXPRAY™/ DROPEX^{PLUS}					
		Raman					
		GC/TID	0	-	6	"	6
		EPA Method 8332(1)	0	-	6	"	6
		MCAWW 353.2(1)	0	"	6	"	6

Notes:
(1) Separate laboratory- STL Sacramento, Ca

CRREL – Cold Regions Research and Engineering Laboratory; RDX – Cyclotrimethylenetrinitramine; MCAWW – Methods for the Chemical Analysis of Wastewater; mg/kg

3.0 REFERENCE TEST METHODS

The reference methods 8330/8332 and 353.2 are generally accepted to be the standard methods of analyses for Nitrocellulose and Nitroglycerin. These methods were typically designed to be used to determine the concentrations of these analytes in soil, water and sludge. When used to analyze these analytes in these matrices they have been proven to work rather well, but even under the best circumstances each of the methods is prone to hindrances due to matrix interferences which cause poor sample extraction or inaccurate and imprecise analysis results. It was not within the scope of this project to validate the reference methods, but to compare the field method performance to the results obtained by the reference methods. As a part of this study samples of various substrates; soil, wallboard, wood and cement were spiked with various concentrations of NC, NG and a combination of NC and NG. The samples were submitted to an outside laboratory for standard laboratory analysis using the reference methods. The resulting data was compared to the concentrations of the spike values added to the matrices for each analysis. The percent recovery for the reference methods are found along with the field method data in Tables 4-6 through 4-9 in Section 4-3 and 4-4. Percent recoveries varied between the different analyses and substrates, but in all cases with the exception of nitroglycerine in cement the analytes were detected, quantifiable and produced useable calibration curves for all of the sample matrices using the reference methods. The concentrations determined from the reference methods were plotted against the known spike concentrations to determine a calibration curve to compare verification/test samples using the reference and field methodologies.

Field test method results will be compared in the following sections with results from the conventional fixed-laboratory analyses of homogenous replicate samples submitted to STL. One set each of the 20-gram samples for each test group was packed into a cooler at 4°C and submitted for quantitative analysis by the reference methods MCAWW 353.2 for NC and/or EPA SW-846 8330/8332 for nitroglycerine.

MCAWW 353.2 Methodology

MCAWW 353.2 method is a colorimetric method that is used to determine nitrate, nitrite, each singularly, or a combination thereof. The method has been adapted for NC determination in the form of nitrate plus nitrite in waters, soils, and sediments. Solid samples are washed initially with methanol and water, agitated on a shaker, centrifuged, and then decanted. The residue is then extracted with acetone, agitated on a shaker, centrifuged, and decanted. The acetone extracts are treated with sodium hydroxide and hydrolyzed. Once hydrolyzed, the extract is filtered and analyzed colorimetrically on an automated colorimetric instrument using the MCAWW 353.2 method.

The method is specific for the analysis of NC in a sample. The method pre-extraction steps with methanol and water remove inorganic forms of nitrate and nitrite as well as nitroglycerin from the sample. NC is insoluble in these solvents and is subsequently removed from the solid matrix in an acetone solvent extraction. The acetone extract is then hydrolyzed to remove NC compound nitro groups and produce inorganic nitrite and nitrate ions. The nitrate ions are then reduced to nitrite with a cadmium column and the total nitrite content is quantified colorimetrically after reaction with a reagent to produce a highly colored species that is a pink-red color.

EPA SW-846 8330/8332 Methodology

EPA SW-846 Method 8330/8332 is a high-performance liquid chromatography (HPLC)/ultraviolet method for the extraction and detection of explosive residues in waters, soils and sediments. Samples are analyzed on an HPLC with a reverse-phase column at an ultraviolet detection of 250 nanometers (nm). Solid sample are air-dried, ground, sieved through a 30-mesh screen, extracted with acetonitrile, treated with calcium chloride solution, filtered, and analyzed by HPLC.

Results from the reference laboratory methods are incorporated into the appropriate sections below for comparison with the field method test results.

4.0 TEST METHODS AND RESULTS

4.1 Qualitative Sample Screening Using Raman Spectroscopy

Introduction/Narrative

The prepared samples were analyzed for the presence of NC and NG by Raman spectroscopy using a portable Raman spectrometer and comparing the scans to reference scans for NC and NG. Reference spectra of NC and NG were obtained and primary peak responses were identified for use in detecting the compounds in the samples. Analyses were then performed on the samples to determine if the identified peak responses were detectable. Sample analyses were performed in three manners:

1. By analyzing the sample matrix directly using an attached fiber videoscope to target the Raman laser for surface spot analysis

2. By analyzing the sample bulk matrix through a glass sample bottle using a sample holder

3. By analyzing 1:1 acetone: sample (volume to weight) extracts of the sample in a glass sample bottle.

Sample analyses included background matrix analyses, which corresponded to the zero (0) concentration spiked samples, and the high concentration individual NC- and NG-spiked samples. For the NG-spiked samples the high concentration was 400 mg/kg, and for the NC-spiked samples the high concentration was 40,000 mg/kg. The spiked NC and NG was not detected in the high concentration samples with the exception of a targeted NC film deposit analysis, which is discussed below; because of this, additional analyses of the lower concentration spiked samples were not performed.

Instrumentation

Raman spectrometer:	InPhotote™ (InPhotonics, Inc., Norwood, Massachusetts)
Raman probe:	Standard fiber RamanProbe™ (InPhotonics, Inc.)
Probe focal length:	5 millimeters (mm)
Fiber length:	5 meters
Excitation laser:	Stabilized 785-nm diode laser with 0.1-nm line width, 300 milliwatt output
Detector:	Vacuum sealed thermoelectric-cooled charge-coupled device array, 45ºC below ambient temperature (-25ºC)
Spectral range:	250 to 1,800 centimeters $(cm)^{-1}$ (Stokes)
Spectral resolution:	4 -6 cm^{-1}
Remote fiber videoscope:	Olympus IPLEX MX (Olympus Corporation)
Fiber length:	10 meters
Fiber focal length:	10 mm

Figure 4-1. Raman Spectroscopy Setup

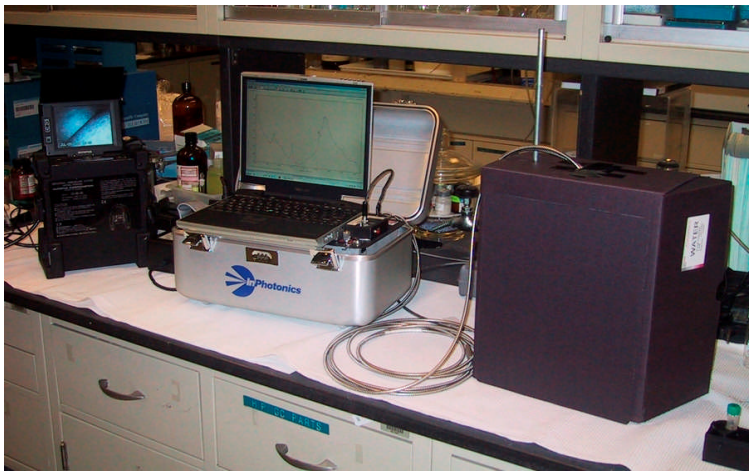
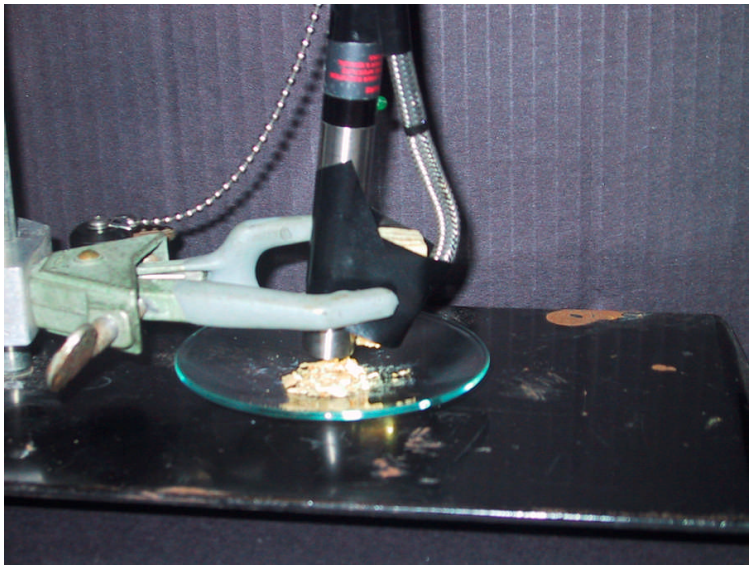


Figure 4-1 shows the instrument setup with videoscope on the left and a direct reading sample enclosure on the right of the Raman spectrometer with attached laptop computer. Direct Raman analysis of the sample matrix surface was aided by attaching the fiber videoscope probe to the Raman probe. The videoscope fiber was attached at an angle of approximately 40 degrees so the Raman excitation laser focal point would be in the field of view. This aided targeting of the laser onto selected points or particles on the surface of the sample for analysis (Figure 4-2).

Figure 4-2. Laser/Videoscope Setup



Direct analyses were performed in a enclosure to shield outside radiation interference. A ring stand in the enclosure was used to clamp the attached videoscope and Raman probe unit in position directed downward at the sample, which was distributed on a watchglass. The Raman probe was clamped at a distance of about 5 mm from the sample surface for analysis. Figure 4-2 shows the probe setup and the sample placement on the watchglass.

Acetone extracts and bulk matrix samples were analyzed in glass sample vials using a supplied sample vial holder. The holder mounted the Raman probe perpendicular to and against the side of the vial to direct the laser into the bulk sample in the vial. The holder also enclosed the sample vial and probe to shield external radiation.

Method

Reference spectra of NC and NG were obtained from material used to prepare sample spike solutions. The NC was white flake material with isopropyl alcohol dampening (Hercules, Inc.) and was determined to be 71 percent solids. NG was obtained by evaporating the 10-milligram per milliliters NG in methanol standard solution (Accutest Labs) to obtain a small bead of NG

concentrate. The material was analyzed directly using the fiber videoscope to target the laser on the material. Figures 4-3 and 4-4 show the spectra obtained for the reference NC and NG, respectively.

Figure 4-3

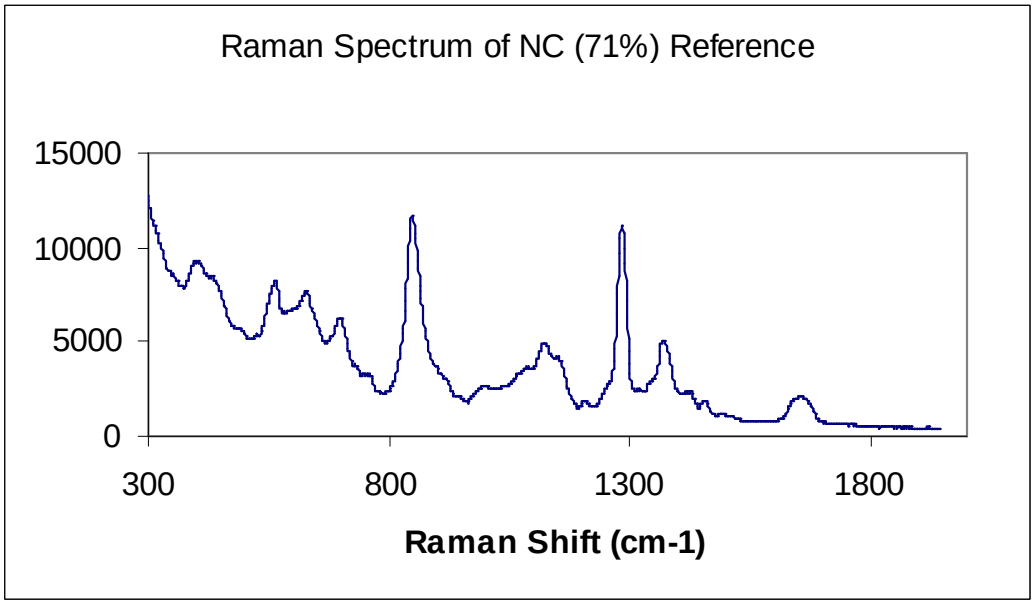
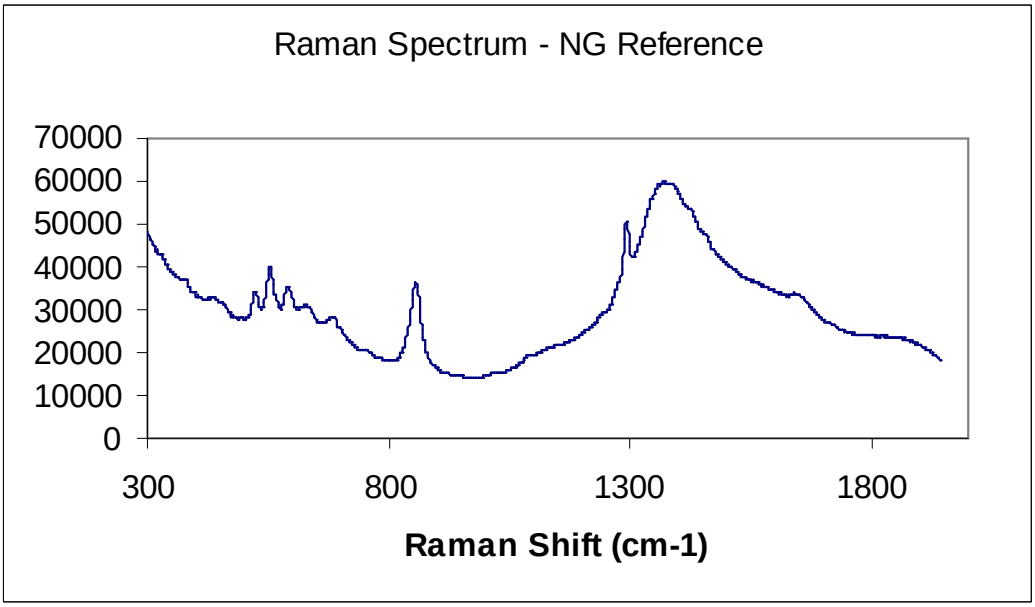


Figure 4-4



The literature (Fell, et al., 1996) lists three peaks for NC within the instrument's spectral range: at 1,282, 847, and 1,373 cm^{-1}. The NC spectra obtained from the reference material matched well with the literature data. The spectra for the NG material also had two primary sharp peaks that matched the two primary peaks for NC at about 850 and 1,280 cm^{-1}. These two peak responses were used to identify the presence of NC or NG in the samples.

Results

A run log of samples analyzed and the results obtained is presented in Table 4-1. Neither NC nor NG was detected in any of the bulk matrix analyses of samples that were spiked with the highest concentrations. The NC/NG peaks were only detected on one surface sample a wood sample spiked with the highest concentration of NC at 40,000 mg/kg (BS-NC-WDB008). The NC was only detected when the Raman laser was focused on a film deposit of NC that was visible against the darker wood surface. Figure 4-5 shows the spectrum that was obtained for that sample with peaks just visible at 850 and 1,280 cm^{-1}.

Figure 4-5

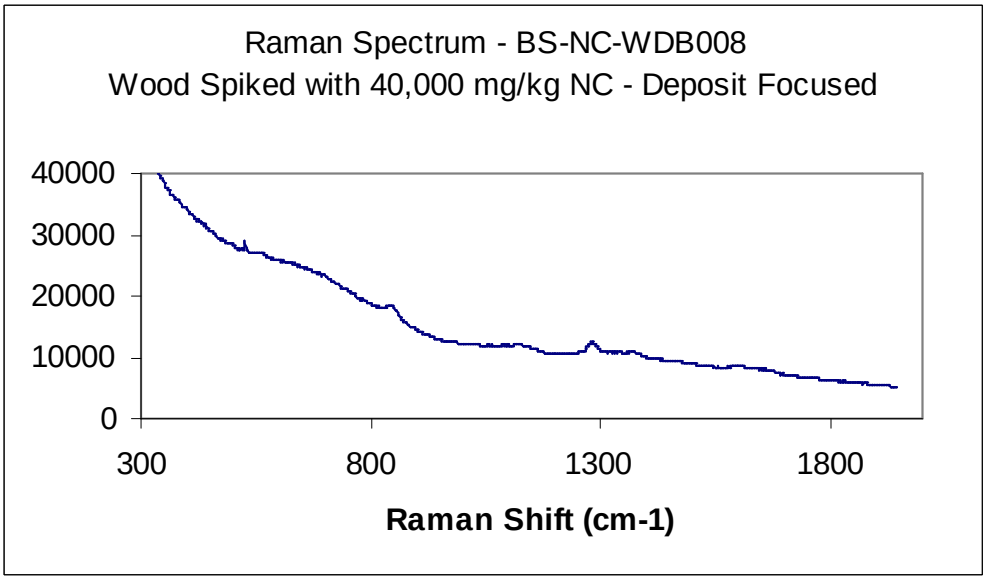
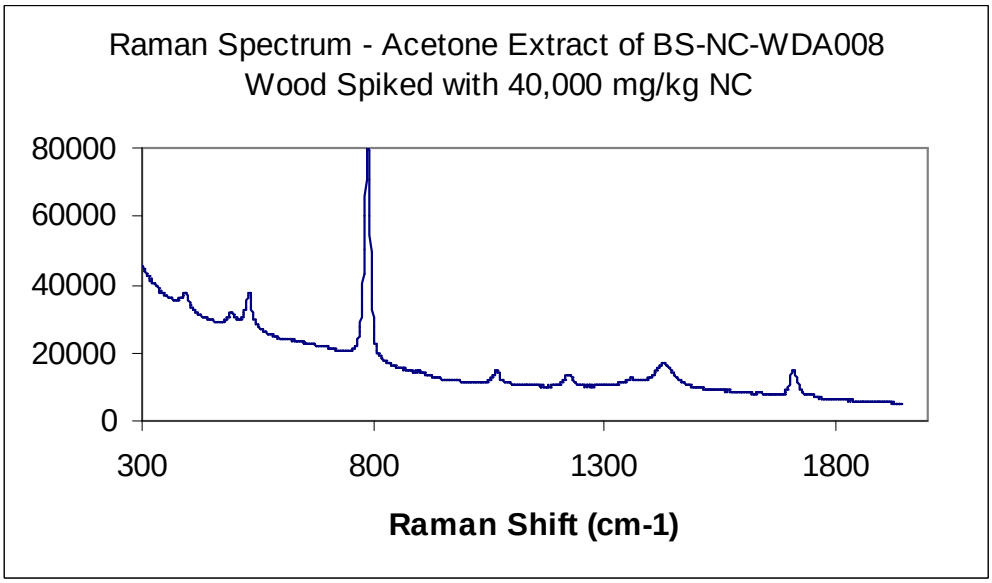


Figure 4-6 shows the Raman scan for the acetone extract of the spiked wood sample. The peaks visible in the scan are due to the acetone solvent. No peaks are discernible for NC at 850 or 1,280 cm^{-1}.

Figure 4-6



Figures 4-7a through 4-7d show the Raman laser focused during analysis on each of the sample matrices; wood, soil, wallboard, and cement, respectively. These pictures were captured with the videoscope that was attached to the Raman probe.

Figure 4-7a. Wood

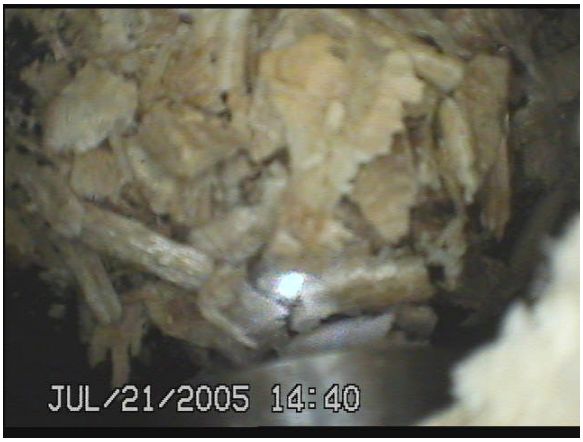


Figure 4-7b. Soil

Figure 4-7c. Wallboard

Figure 4-7d. Concrete

During some of the analyses on the darker wood or soil matrices the sample was burned by the focused energy of the Raman laser and smoke trails from the sample were occasionally visible. Figure 4-8 shows a wood matrix with smoke visible from the laser spot Figures 4-8a and 4-8b show a soil particle that was charred by the laser.

Figure 4-8. Wood Being Burned by Laser

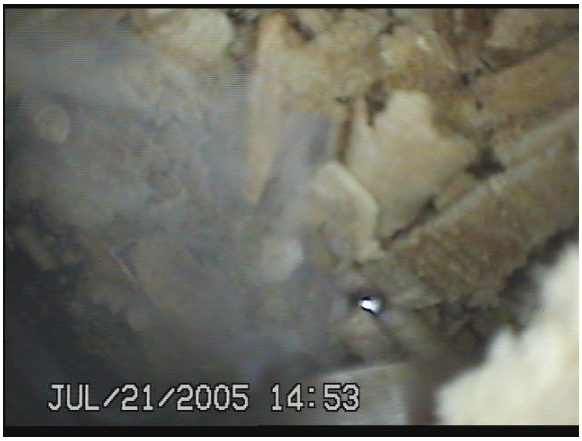
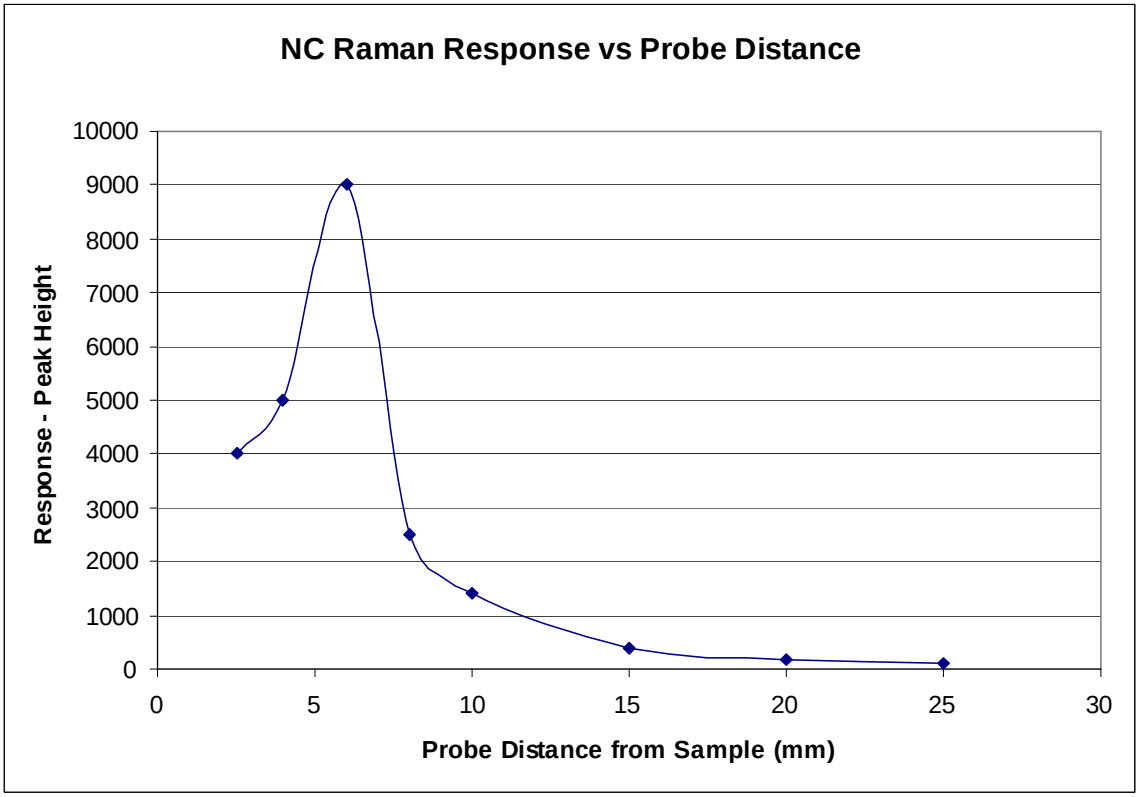


Figure 4-8a. Soil Analysis

Figure 4-8b. Soil Burned by Analysis

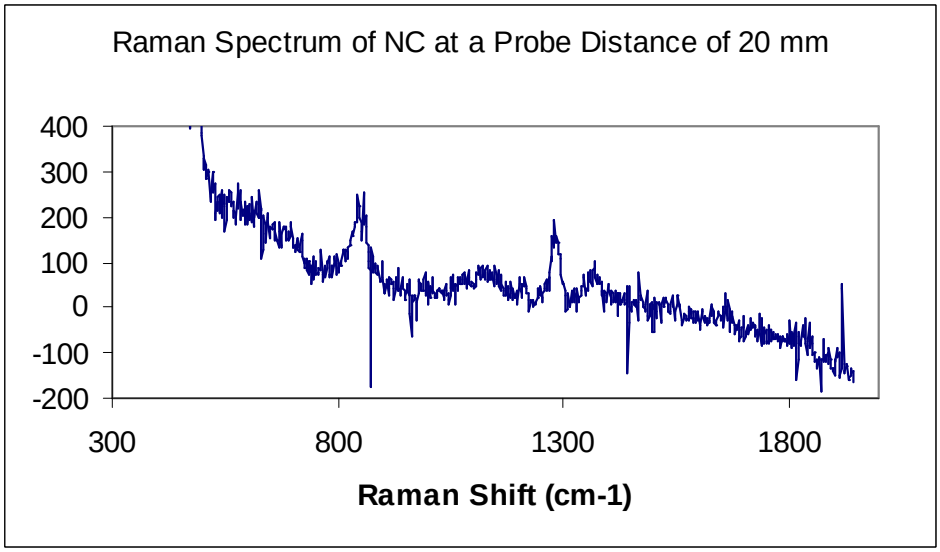
The effect of distance between the Raman probe and the sample surface was investigated to evaluate the impact on analyte response. The usefulness of Raman spectroscopy for remote analysis of NC and NG deposits depends on how critical the probe-to-sample distance is to analyte detection. If the distance requirement cannot be easily controlled by remote operations, then false negative results may be obtained. To evaluate the distance impact, Raman scans were taken of NC flake material with the probe located at distances ranging from about 2 mm to 30 mm. The signal response for the NC peaks (peak heights) at 850 and 1,280 cm^{-1}, which are approximately equal, were recorded and plotted as a function of the probe distance. The tabulated results are included in Table 4-1 and the plot results are shown on Figure 4-9.

Figure 4-9



The plot shows that the Raman signal for NC is sensitive to the probe distance from the sample with the signal peaking at a distance of 5 to 6 mm and then dropping off sharply to less than 10 percent of the peak signal at a distance of 15 mm. Figure 4-10 shows the Raman spectrum of NC collected at a probe distance of 20 mm and illustrates that the response signals at 850 and 1,280 cm^{-1} are approaching the limit of detection. These data suggest that remote Raman analysis may present false negatives if the probe position relative to the sample cannot be carefully controlled and monitored with a tolerance on the order of 1 to 2 mm. An attached fiber videoscope similar to the one used in this work should be used to visually assure that the incidence of the Raman excitation laser is properly focused on the desired sample location.

Figure 4-10



Conclusion

- Raman spectroscopy was not useful for the analysis of the bulk sample matrices for the presence of NC at concentrations up to 40,000 mg/kg or for the presence of NG at concentrations up to 400 mg/kg.

- Extracting the sample matrices with acetone and analyzing the extracts by Raman spectroscopy was also not effective for detecting NC and NG at the highest concentrations investigated.

- Analysis of visible deposits of NC and NG may be performed by Raman spectroscopy for qualitative identification, providing sufficient material is available and the Raman probe can be properly positioned for analysis.

- Probe positioning with respect to the sample surface being analyzed is critical for obtaining a high-quality spectral scan and being able to detect analytes. A fiber videoscope is recommended for targeting the Raman probe for sample analysis.

- Darker sample matrices may absorb enough of the Raman excitation laser energy to be burned or charred during analysis and it is possible that energetic material in close proximity may be ignited.

Table 4-1
Raman Sample Analysis Run Log and Results Summary

Sample	NC Spike Conc (mg/kg)	Type	Method	Power	Scan Time (Sec)	Date Analyzed	Result
Acetone	0	Solvent	Glass Vial	Full	5	21-Jul	Bkgd
Acetone	0	Solvent	Glass Vial	Full	20	21-Jul	Bkgd
Acetone	0	Solvent	Glass Vial	Full	50	21-Jul	Bkgd
Acetone	0	Solvent	Glass Vial	Full	100	21-Jul	Bkgd
BS-NC-WDB001	0	Matrix	Glass Vial	Full	100	27-Jun	ND
BS-NC-WDB008	40,000	Matrix	Bare	Full	100	20-Jul	ND
BS-NC-WDB008b	40,000	Matrix	Bare	Full	100	20-Jul	ND
BS-NC-WDB008	40,000	Matrix	Glass Vial	Full	100	20-Jul	ND
BS-NC-WDB008b	40,000	Matrix	Glass Vial	Full	100	20-Jul	ND, D[a]
BS-NC-WDB008	40,000	1:1 Acetone Ext.	Glass Vial	Full	100	21-Jul	ND
BS-NC-WBB001	0	Matrix	Glass Vial	Full	100	27-Jun	ND
BS-NC-WBB008	40,000	Matrix	Bare	Full	100	20-Jul	ND
BS-NC-WBB008	40,000	Matrix	Glass Vial	Full	100	20-Jul	ND
BS-NC-WBB008	40,000	1:1 Acetone Ext.	Glass Vial	Full	100	21-Jul	ND
BS-NC-CMB001	0	Matrix	Glass Vial	Full	100	27-Jun	ND
BS-NC-CMB008	40,000	Matrix	Bare	Full	100	20-Jul	ND
BS-NC-CMB008	40,000	Matrix	Bare	Full	200	20-Jul	ND
BS-NC-CMB008	40,000	Matrix	Glass Vial	Full	100	20-Jul	ND
BS-NC-CMB008	40,000	1:1 Acetone Ext.	Glass Vial	Full	100	21-Jul	ND
BS-NC-SSB001	0	Matrix	Glass Vial	Full	100	27-Jun	ND
BS-NC-SSB008	40,000	Matrix	Bare	Full	100	20-Jul	ND
BS-NC-SSB008	40,000	Matrix	Glass Vial	Full	100	20-Jul	ND
BS-NC-SSB008	40,000	1:1 Acetone Ext.	Glass Vial	Full	100	25-Jul	ND
BS-NC-SSB008b	40,000	1:1 Acetone Ext.	Glass Vial	Full	100	25-Jul	ND

[a]Detected only when laser was focused on a visible NC film deposit.

Table 4-1. (continued)

Sample	NG Spike Conc (mg/kg)	Type	Method	Power	Scan Time (Sec)	Date Analyzed	Result
BS-NG-WDB015	0	Matrix	Bare	Full	100	14-Jul	ND
BS-NG-WDB015	0	Matrix	Glass Vial	Full	100	27-Jun	ND
BS-NG-WDB020	400	Matrix	Glass Vial	Full	100	14-Jul	ND
BS-NG-WDB020	400	Matrix	Bare	Full	100	14-Jul	ND
BS-NG-WDB020	400	Matrix	Bare	Full	75	14-Jul	ND
BS-NG-WDB020b	400	Matrix	Bare	Full	100	14-Jul	ND
BS-NG-WDB020	400	1:1 Acetone Ext.	Glass Vial	Full	100	21-Jul	ND
BS-NG-WBB015	0	Matrix	Bare	Full	100	20-Jul	ND
BS-NG-WBB015	0	Matrix	Glass Vial	Full	100	27-Jun	ND
BS-NG-WBB015	0	Matrix	Glass Vial	Full	100	14-Jul	ND
BS-NG-WBB020	400	Matrix	Glass Vial	Full	100	14-Jul	ND
BS-NG-WBB020b	400	Matrix	Glass Vial	Full	100	14-Jul	ND
BS-NG-WBB020	400	1:1 Acetone Ext.	Glass Vial	Full	100	21-Jul	ND
BS-NG-CMB015	0	Matrix	Glass Vial	Full	100	27-Jun	ND
BS-NG-CMB015	0	Matrix	Bare	Full	100	12-Jul	ND
BS-NG-CMB020	400	Matrix	Bare	Full	100	12-Jul	ND
BS-NG-CMB020	400	Matrix	Glass Vial	Full	100	12-Jul	ND
BS-NG-CMB020	400	1:1 Acetone Ext.	Glass Vial	Full	100	21-Jul	ND
BS-NG-SSB015	0	Matrix	Glass Vial	Full	100	27-Jun	ND
BS-NG-SSB015	0	Matrix	Bare	Full	100	12-Jul	ND
BS-NG-SSB020	400	Matrix	Bare	Full	100	12-Jul	ND
BS-NG-SSB020	400	Matrix	Glass Vial	Full	400	6-Jul	ND
BS-NG-SSB020b	400	Matrix	Glass Vial	Full	400	6-Jul	ND
BS-NG-SSB020	400	1:1 Acetone Ext.	Glass Vial	Full	100	21-Jul	ND

Table 4-1. (continued)

Sample	Spike Conc (mg/kg)	Type	Method	Power	Scan Time (Sec)	Date Analyzed	Result	Peak Ht	Probe Distance (mm)
NG Spike Evap	>80%	Concentrated	Bare	60	100	21-Jul	Reference	NA	5
NG Spike Evap	>80%	Concentrated	Bare	80	100	21-Jul	Reference	NA	5
NG Spike Evap	>80%	Concentrated	Bare	100	100	21-Jul	Reference	NA	5
NG Spike Evap	>80%	Concentrated	Bare	100	100	25-Jul	Reference	NA	5
NG Spike Evap	>80%	Concentrated	Bare	100	100	29-Jul	Reference	NA	5
Methanol	100%	Solvent	Glass Vial	100	100	24-Jun	Bkgd	NA	5
Methanolb	100%	Solvent	Glass Vial	100	100	21-Jul	Bkgd	NA	5
NC Flake	71%	Solid, flake	Bare	100	100	24-Jun	Reference	NA	5
NC Flake	71%	Solid, flake	Bare	100	100	27-Jun	Reference	NA	5
Distance Study:									
NC Flake	71%	Solid, flake; 2-3 mm	Bare	10 0	100	28-Jul	Reference	4000	2.5
NC Flake	71%	Solid, flake; 4 mm	Bare	100	100	28-Jul	Reference	5000	4
NC Flake	71%	Solid, flake; 6 mm	Bare	100	100	28-Jul	Reference	9000	6
NC Flake	71%	Solid, flake; 8 mm	Bare	100	100	28-Jul	Reference	2500	8
NC Flake	71%	Solid, flake; 10 mm	Bare	100	100	28-Jul	Reference	1400	10
NC Flake	71%	Solid, flake; 15 mm	Bare	100	100	28-Jul	Reference	400	15
NC Flake	71%	Solid, flake; 20 mm	Bare	100	100	28-Jul	Reference	160	20
NC Flake	71%	Solid, flake; 25 mm	Bare	100	100	28-Jul	Reference	100	25
NC Flake	71%	Solid, flake; 30 mm	Bare	100	100	28-Jul	Reference	<100	30

mg/kg – milligrams per kilogram; NP – Nondetect; NA – Not applicable; NC – Nitrocellulose; NG – Nitroglycerine.

4.2 Qualitative Sample Screening Using EXPRAY™ and DROPEX^{PLUS}

Introduction/Narrative

EXPRAY™ and DROPEX^{PLUS} colorimetric test kits were used to screen prepared extracts of the spiked materials for the presence of NC and NG. Both test kits are designed to provide immediate detection of explosives (including NC and NG) by application of supplied reagents in a specified sequence. Reference materials were first analyzed to obtain an indication of response for both NC and NG. Analyses were then performed on the prepared sample extracts to determine at what level a color change was detectable.

Materials

EXPRAY™ and DROPEX^{PLUS} colorimetric test kits were both purchased from Medimpex United, Inc. Both systems are based on the same reagents but are in different delivery form, i.e., spray can vs. dropper bottles. Each test kit is supplied with 2–inch-by-3-inch collection papers to perform the test; however, for comparison purposes an initial study was conducted to determine if a qualitative filter paper larger in size would provide the same reaction as the test kit paper and allow for testing multiple samples on the same test paper. A set of prepared NG standards were spotted on two different 15-cm Whatman filters, a Whatman No. 40 and a Whatman No. 1, and on the supplied EXPRAY™/ DROPEX^{PLUS} paper. The test results showed that a Whatman No. 1 filter expressed the same sensitivity as the test kit paper performing slightly better than the Whatman No. 4 paper. The larger test paper allows multiple samples from one test group to be tested side-by-side for ease of comparison and documentation of results. Figure 4-11 shows EXPRAY™ testing of NG reference standards at multiple concentrations.

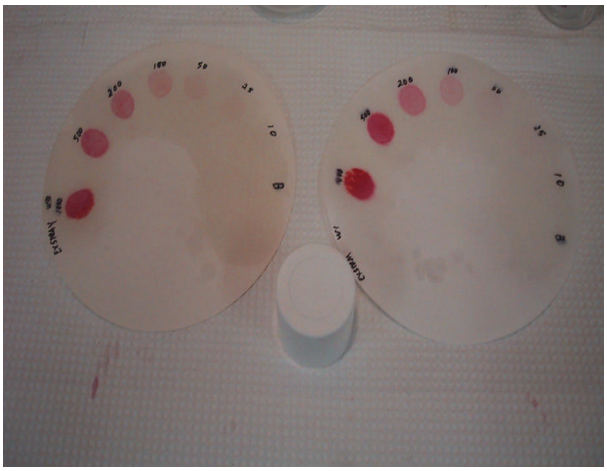


Figure 4-11. Spiked Reference Materials

Method

For each sample a 20-gram sample aliquot was extracted by gently shaking 1.5 hrs with a 1:1 weight to volume ratio of sample to acetone. Due to absorption and the bulk of the sample, 70 milliliters (mL) of acetone (3.5 ratio) was required to extract the wood aliquots and 30 mL (1.5 ratio) was required to extract the wallboard. After extraction, the sample was allowed to settle prior to filtering. The extract was transferred to a 10-mL syringe, filtered into amber vials, and stored at 4°C pending analysis. Tests were performed using 10 microliters (µLs) of extract placed onto the 15-cm filter paper using a 10-µL glass syringe and allowing it to air dry.

Using the EXPRAY™ kit the spray bottle labeled EXPRAY™ No. 1 was applied briefly at a distance of about 15 cm. The same area was then sprayed with the EXPRAY™ No. 2 can until slightly damp. In cases where NC or NG was detected, color change to pink or red was completed in seconds.

The DROPEX^{PLUS} kit was tested identical to the EXPRAY™ using the same extracts. A couple of drops of Reagent No. 1 were spotted on the extract aliquot on the filter. Approximately 15 seconds later, a couple of drops of Reagent No. 2 were added. If the test was positive for NC or NG, color change to red or pink was noted immediately as pictured on Figure 4-12 and Figure 4-13.

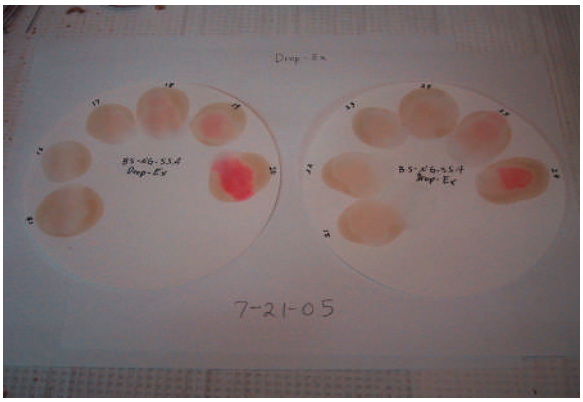


Figure 4-12. DROPEX^{PLUS} on Soil

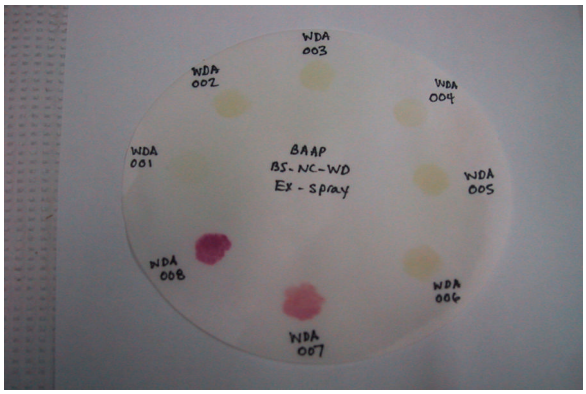


Figure 4-13. EXPRAY™ on Wood

Results

The test kit results for the sample analyses are shown in Table 4-3. The results were recorded as either a positive (+) or negative (-) test response. In some cases, sample concentrations near the detectable limit for the method gave a positive result that was only faintly discernable, but in general, the test response was increasingly more intense as the test NC or NG concentration increased above the detectable limit. Detectable limits of spiked NC and NG material for each test matrix are summarized in Table 4-2. The values represent the lowest concentration of both the calibration and verification samples at which a positive response was obtained.

Both test kits were also tested at 4°C to evaluate low temperature effects on the performance of the test kits. The test kits were placed in a walk-in cooler overnight. The test on the NG soil test group was then repeated inside the cooler with the chilled reagents. Both test kits seemed to work equally well and correlate well with the results obtained at room temperature (21°C). These results are indicated in the tables below, alongside the original data with a ++ for positive detection at both temperatures. DROPEX^{PLUS} performed slightly better than EXPRAY™, with detections at 40 and 80 mg/kg, respectively.

Both test kits seemed to work equally well and correlate well with the reference method, STL 8330/8332, with limitations based on detectable concentration limits for each matrix, which were matrix dependent. Except for three test results, sample concentrations above the method's detectable limit were all positive. The three false negative results were for sample concentrations near but just above the detectable limit. As noted above, the test responses were faint for concentrations near the detectable limit, so a false negative near the limit can result from a slight variation in test conditions or performance. Of the three false negative results, one was with EXPRAY™ and two were with DROPEX^{PLUS}. For sample concentrations below the detectable limit, all results were negative. These could be considered false negatives (except for unspiked

background samples) if the detectable limit is not realized. All unspiked background matrix samples gave negative results, so there were no false positives.
The DROPEX^{PLUS} test had lower detectable limits for NC on three of the four sample matrices: soil, wallboard, and wood. NG EXPRAY™ had a lower detectable limit for wallboard, while DROPEX^{PLUS} had a lower detectable limit for wood. For the combined NC and NG spiked samples, the DROPEX^{PLUS} test had lower detectable limits on two of the four sample matrices: wood and cement.

Soil
The soil matrix gave the lowest detectable limits for NC and NG. This is due at least in part to the ability to use a low ratio (1:1) of solvent to matrix for sample extraction. The DROPEX^{PLUS} test had a slightly lower detectable limit for NC (100 mg/kg) than EXPRAY™ (250 mg/kg), but for NG the detectable limits were the same at 40 mg/kg. The detectable limits for the combined NC and NG test samples were also the same at 250 mg/kg NC with 25 mg/kg NG. There were no false negatives.

Wallboard
The detectable limits for NC and NG on wallboard were higher than those for soil. This is due at least in part to the use of a higher ratio (1.5:1) of solvent to matrix for sample extraction. The DROPEX^{PLUS} test had a slightly lower detectable limit for NC (250 mg/kg) than EXPRAY™ (400 mg/kg), but for NG the EXPRAY™ test had a slightly lower detectable limit of 80 mg/kg than EXPRAY™'s 250 mg/kg. The detectable limits for the combined NC and NG test samples were the same at 250 mg/kg NC with 25 mg/kg NG. There was one false negative with EXPRAY™ for the 100 mg/kg NG calibration sample. The concentration is greater than the 80 mg/kg concentration that was just detected in a verification sample. These results suggest that the confidence for detecting NG on wallboard with EXPRAY™ at the 80 to 100 mg/kg concentration range is not high.

Wood
The detectable limits for NC and NG on wood were also higher than those for soil. This is due at least in part to the use of a higher ratio (3.5:1) of solvent to matrix for sample extraction. The extract also had a yellow color, which interfered somewhat with detection of the pink-red color development for positive NC/NG indication. The DROPEX^{PLUS} test had a lower detectable limit for NC (250 mg/kg) than EXPRAY™ (2,500 mg/kg). The DROPEX^{PLUS} test also had a lower detectable limit for NG (80 mg/kg) than EXPRAY™ (250 mg/kg). The detectable limits for the combined NC and NG test samples were 4,000 mg/kg NC with 400 mg/kg NG for EXPRAY™ and 1,000 mg/kg NC with 100 mg/kg NG for DROPEX^{PLUS}. There were two false negatives with DROPEX^{PLUS}: one for the 400 mg/kg NC calibration sample and one for the 100 mg/kg NG calibration sample. These concentrations are greater than the 250 mg/kg NC and 80 mg/kg NG concentrations that were just detected in verification samples. These results suggest that the confidence for detecting NG at the 80 to 100 mg/kg concentration range and NC at the 250 to 400 mg/kg concentration range on wood with DROPEX^{PLUS} is not high.

Cement
The detectable limit for NC was the same for both tests (250 mg/kg). Neither test detected NG at any of the sample concentrations. This was consistent with results from the reference method (STL 8330/8332), which indicated NG was not present on the matrix at a significant

concentration even for the highest concentration spiked samples. A search of the literature revealed that energetic compounds are hydrolyzed under alkaline conditions to free inorganic nitrate and nitrite ions and lower molecular weight organic fragments (Su, 1996). The degree of organic degradation depends on the hydrolysis conditions. It is believed that the alkaline conditions in the cement matrix may have caused hydrolysis of the NG that was spiked onto the matrix. Thorne, et al. (2004) explains that energetic compounds may be treated on soil by the addition of lime, which is a major component of cement. The conditions in the cement matrix; however, did not seem to impact NC detection, which suggests that NC is more difficult to hydrolyze than NG.

The detectable limits for the combined NC and NG test samples were 1,000 mg/kg NC with 100 mg/kg NG spike for EXPRAY™ and 250 mg/kg NC with 25 mg/kg NG spike for DROPEX^{PLUS}. Despite the nondetection of NG, it was considered that there were no false negatives, since NG was not detected by the reference method.

Conclusion

- EXPRAY™ and DROPEX^{PLUS} were effective in detecting NC and NG in the matrices (except NG in cement) with results consistent with the STL 8330/8332 reference method as long as concentrations were above detectable limits determined by these tests.

- EXPRAY™ and DROPEX^{PLUS} were effective in detecting NC and NG in the matrices at 4°C, with comparable results to those obtained at 21°C.

- NG was not detected in the cement matrix and this is believed to be due to hydrolysis degradation caused by the alkaline nature of the matrix. The results were consistent with results from the reference method for NG.

- Detectable limits were affected by the ratio of solvent to sample that was necessary to get complete matrix wetting for extraction. Wood matrix required a 3.5:1 ratio of acetone volume to sample weight. Wallboard required a ratio of 1.5:1. For soil and cement, a ratio of 1:1 was used.

- NC detectable limits ranged from 250 mg/kg on soil to 2,500 mg/kg for wood using EXPRAY™ and 100 mg/kg on soil to 250 mg/kg on wood using DROPEX^{PLUS}.

- NG detectable limits (excluding cement matrix) ranged from 40 mg/kg on soil to 250 mg/kg for wood using EXPRAY™ and 40 mg/kg on soil to 250 mg/kg on wallboard using DROPEX^{PLUS}.

- The NC and NG combined tests had slightly higher detectable limits ranging from 250 mg/kg NC with 25 mg/kg NG on soil to 4,000 mg/kg NC with 400 mg/kg NG on wood.

- DROPEX^{PLUS} had somewhat lower detectable limits than EXPRAY™ for NC and combined NC and NG.

- Detectable limits for NG were comparable for both EXPRAY™ and DROPEX^{PLUS}.

- Three false negatives were obtained (one EXPRAY™ and two DROPEX^{PLUS}) out of a possible 91 tests that had concentrations above the detectable limits. The detectable limits were defined as the lowest concentration detected for each matrix. The three false negatives were for tests with concentrations just above the lowest detectable concentration observed for the matrix, and the test responses were faint near the detectable limit.

- No false positive results were obtained.

Table 4-2
Detectable Limits EXPRAY™/ DROPEX^{PLUS}

Soil Extracts

Spike Material	EXPRAY™ Detectable Limit mg/kg	DROPEX^{PLUS} Detectable Limit mg/kg
NC	250	100
NG	40	40
Combined NC/NG	250/25	250/25

Wallboard Extracts

Spike Material	EXPRAY™ Detectable Limit mg/kg	DROPEX^{PLUS} Detectable Limit mg/kg
NC	400	250
NG	80	250
Combined NC/NG	250/25	250/25

Wood

Spike Material	EXPRAY™ Detectable Limit mg/kg	DROPEX^{PLUS} Detectable Limit mg/kg
NC	2500	250
NG	250	80
Combined NC/NG	4000/400	250/400

Table 4-2 (continued)
Detectable Limits EXPRAY™/ DROPEX^{PLUS}

Cement

Spike Material	EXPRAY™ Detectable Limit mg/kg	DROPEX^{PLUS} Detectable Limit mg/kg
NC	250	250
NG	ND	ND
Combined NC/NG	1000/100	250/25

NG – Nitroglycerine; NC – Nitrocellulose; mg/kg – milligrams per kilogram.

Table 4-3
DROPEX^{PLUS} /EXPRAY™ Test Kit Results

Sample Identification	Matrix	NC Spike Concentration mg/kg	STL MCAWW 353.2 NC mg/kg	Expray NC	Drop-Ex NC		Sample Identification	Matrix	NC Spike Concentration mg/kg	STL MCAWW 353.2 NC mg/kg	Expray NC	Drop-Ex NC
BS-NC-SSB001	Soil	0	1.4 B	-	-		BS-NC-WDB001	Wood	0	14.2	-	-
BS-NC-SSB002	Soil	5	2.8	-	-		BS-NC-WDB002	Wood	5	12.2	-	-
BS-NC-SSB003	Soil	20	10.9	-	-		BS-NC-WDB003	Wood	20	15.5	-	-
BS-NC-SSB004	Soil	50	28.9	-	-		BS-NC-WDB004	Wood	50	25.2	-	-
BS-NC-SSB005	Soil	100	26.3	-	+		BS-NC-WDB005	Wood	100	31.7	-	-
BS-NC-SSB006	Soil	400	125	+	+		BS-NC-WDB006	Wood	400	166	-	-
BS-NC-SSB007	Soil	4000	2600	+	+		BS-NC-WDB007	Wood	4000	2020	+	+
BS-NC-SSB008	Soil	40000	11200	+	+		BS-NC-WDB008	Wood	40000	21100	+	+
BS-NC-SSB009	Soil	0	4.1	-	-		BS-NC-WDB009	Wood	0	14.2	-	-
BS-NC-SSB010	Soil	2.5	3	-	-		BS-NC-WDB010	Wood	2.5	17.5	-	-
BS-NC-SSB011	Soil	10	2.8	-	-		BS-NC-WDB011	Wood	10	16.2	-	-
BS-NC-SSB012	Soil	80	24.1	-	-		BS-NC-WDB012	Wood	80	33.9	-	-
BS-NC-SSB013	Soil	250	170	+	+		BS-NC-WDB013	Wood	250	180	-	+
BS-NC-SSB014	Soil	2500	1530	+	+		BS-NC-WDB014	Wood	2500	1250	+	+
BS-NC-WBB001	Wallboard	0	27.3	-	-		BS-NC-CMB001	Cement	0	2.7	-	-
BS-NC-WBB002	Wallboard	5	2.6	-	-		BS-NC-CMB002	Cement	5	6.2	-	-
BS-NC-WBB003	Wallboard	20	32.8	-	-		BS-NC-CMB003	Cement	20	9.3	-	-
BS-NC-WBB004	Wallboard	50	1.8	-	-		BS-NC-CMB004	Cement	50	21.6	-	-
BS-NC-WBB005	Wallboard	100	48.5	-	-		BS-NC-CMB005	Cement	100	85.7	-	-
BS-NC-WBB006	Wallboard	400	135	+	+		BS-NC-CMB006	Cement	400	256	+	+
BS-NC-WBB007	Wallboard	4000	1810	+	+		BS-NC-CMB007	Cement	4000	1840	+	+
BS-NC-WBB008	Wallboard	40000	14300	+	+		BS-NC-CMB008	Cement	40000	19500	+	+
BS-NC-WBB009	Wallboard	0	31.9	-	-		BS-NC-CMB009	Cement	0	3.6	-	-
BS-NC-WBB010	Wallboard	2.5	33	-	-		BS-NC-CMB010	Cement	2.5	7.9	-	-
BS-NC-WBB011	Wallboard	10	31.5	-	-		BS-NC-CMB011	Cement	10	23.2	-	-
BS-NC-WBB012	Wallboard	80	43.5	-	-		BS-NC-CMB012	Cement	80	40.1	-	-
BS-NC-WBB013	Wallboard	250	107	-	+		BS-NC-CMB013	Cement	250	218	+	+
BS-NC-WBB014	Wallboard	2500	957	+	+		BS-NC-CMB014	Cement	2500	1470	+	+

Table 4-3. (continued)

Sample Identification	Matrix	NG Sample Spike Concentration mg/Kg	STL 8330/8332 NG mg/kg	Expray NG	Drop-Ex NG
BS-NG-SSB015	Soil	0	0	-	-
BS-NG-SSB016	Soil	5	4.7	-	-
BS-NG-SSB017	Soil	20	20	-	-
BS-NG-SSB018	Soil	50	45	+	+
BS-NG-SSB019	Soil	100	96	+	+
BS-NG-SSB020	Soil	400	430	+	+
BS-NG-SSB021	Soil	0	0.5	-	-
BS-NG-SSB022	Soil	2.5	2.1	-	-
BS-NG-SSB023	Soil	10	8.5	-	-
BS-NG-SSB024	Soil	40	41	+	++
BS-NG-SSB025	Soil	80	77	++	++
BS-NG-SSB026	Soil	250	260	++	++

Sample Identification	Matrix	NG Sample Spike Concentration mg/Kg	STL 8330/8332 NG mg/kg	Expray NG	Drop-Ex NG
BS-NG-WDB015	Wood	0	0	-	-
BS-NG-WDB016	Wood	5	11	-	-
BS-NG-WDB017	Wood	20	25	-	-
BS-NG-WDB018	Wood	50	54	-	-
BS-NG-WDB019	Wood	100	96	-	-
BS-NG-WDB020	Wood	400	380	+	+
BS-NG-WDB021	Wood	0	0	-	-
BS-NG-WDB022	Wood	2.5	0	-	-
BS-NG-WDB023	Wood	10	19	-	-
BS-NG-WDB024	Wood	40	28	-	-
BS-NG-WDB025	Wood	80	100	-	+
BS-NG-WDB026	Wood	250	260	+	+

BS-NG-WBB015	Wallboard	0	0	-	-
BS-NG-WBB016	Wallboard	5	2.6	-	-
BS-NG-WBB017	Wallboard	20	10	-	-
BS-NG-WBB018	Wallboard	50	28	-	-
BS-NG-WBB019	Wallboard	100	58	-	-
BS-NG-WBB020	Wallboard	400	250	+	+
BS-NG-WBB021	Wallboard	0	0	-	-
BS-NG-WBB022	Wallboard	2.5	1.3	-	-
BS-NG-WBB023	Wallboard	10	5	-	-
BS-NG-WBB024	Wallboard	40	22	-	-
BS-NG-WBB025	Wallboard	80	34	+	-
BS-NG-WBB026	Wallboard	250	150	+	+

BS-NG-CMB015	Cement	0	0	-	-
BS-NG-CMB016	Cement	5	0	-	-
BS-NG-CMB017	Cement	20	0.087	-	-
BS-NG-CMB018	Cement	50	0.19	-	-
BS-NG-CMB019	Cement	100	0.24	-	-
BS-NG-CMB020	Cement	400	1.2	-	-
BS-NG-CMB021	Cement	0	0	-	-
BS-NG-CMB022	Cement	2.5	0.086	-	-
BS-NG-CMB023	Cement	10	0.45	-	-
BS-NG-CMB024	Cement	40	0.086	-	-
BS-NG-CMB025	Cement	80	0	-	-
BS-NG-CMB026	Cement	250	2.8	-	-

(+)= positive / (++)= Tested at 4°C and 21°C; (-)= negative

Table 4-3. (continued)

Sample Identification	Matrix	Spike Conc mg/Kg NC	Spike Conc mg/Kg NG	STL 8330/8332	STL MCAWW 353.20	Expray	Drop-Ex	Sample Identification	Matrix	Spike Conc mg/Kg NC	Spike Conc mg/Kg NG	STL 8330/8332	STL MCAWW 353.20	Expray	Drop-Ex
BS-CG-SSB027	Soil	0	0	0.013	14.3	-	-	BS-CG-WDB027	Wood	0	0	0.5	6.9	-	-
BS-CG-SSB028	Soil	50	5	0.069	32.5	-	-	BS-CG-WDB028	Wood	50	5	0.5	23.1	-	-
BS-CG-SSB029	Soil	250	25	11	198	+	+	BS-CG-WDB029	Wood	250	25	28	23.1	-	-
BS-CG-SSB030	Soil	1000	100	63	661	+	+	BS-CG-WDB030	Wood	1000	100	84	330	-	+
BS-CG-SSB030D	Soil	1000	100	77	966	+	+	BS-CG-WDB031	Wood	4000	400	300	1710	+	+
BS-CG-SSB031	Soil	4000	400	280	3570	+	+	BS-CG-WDB032	Wood	250	400	210	138	-	+
BS-CG-SSB032	Soil	250	400	290	320	+	+								
BS-CG-WBB027	Wallboard	0	0	0.21	52.1	-	-	BS-CG-CMB027	Cement	0	0	0.5	3.9	-	-
BS-CG-WBB028	Wallboard	50	5	1.1	61.7	-	-	BS-CG-CMB028	Cement	50	5	0.17	26.1	-	-
BS-CG-WBB029	Wallboard	250	25	1.0	103	+	+	BS-CG-CMB029	Cement	250	25	0.23	260	-	+
BS-CG-WBB030	Wallboard	1000	100	8.1	463	+	+	BS-CG-CMB030	Cement	1000	100	2.3	1280	+	+
BS-CG-WBB031	Wallboard	4000	400	150	1640	+	+	BS-CG-CMB031	Cement	4000	400	77	4920	+	+
BS-CG-WBB032	Wallboard	250	400	15	168	+	+	BS-CG-CMB032	Cement	250	400	3.7	322	+	+

STL – Severn Trent Laboratories; MCAWW – Methods for the Chemical Analysis of Wastewater; mg/kg – milligrams per kilogram; NC – Nitrocellulose; NG – Nitroglycerine.

4.3 Quantitative Analysis Using CRREL RDX Method

Introduction/Narrative

Sample extracts of each test group were prepared and analyzed for NC and NG based on CRREL RDX Method 8510 "Colorimetric Screening Procedure for RDX and HMX in Soil" (EPA, 2000) Colored extracts were analyzed in the absorbance mode using a HACH DR/2010 spectrophotometer. Reference standard materials and blanks were analyzed daily to verify instrument response. A calibration curve based on sample response was established using the first eight samples in the NC test groups and the first six samples in the NG test groups. Six test samples for each test group were then analyzed to verify the calibration curves. The impact of NC + NG on the performance of the method was evaluated from the results of analysis of the six samples spiked with a combination of NC and NG.

The CRREL RDX method is a non specific colorimetric method for analysis of NC and NG when both are present in the sample matrix. The method is similar to the MCAWW 353.2 reference method, except that NG is not removed in a pre-extraction step. The method does remove inorganic forms of nitrate and nitrite ion by a column cleanup procedure prior to the hydrolysis step. The method also differs by using an acid hydrolysis step rather than base hydrolysis to convert NG and NC nitrogen (N) to nitrite and nitrate ions. The method then reduces nitrate to nitrite using zinc powder rather than a cadmium column and subsequently generates the same or similar color species for colorimetric quantification. Results may be obtained for the total of NC and NG in terms of either NC or NG depending upon whether the calibration for NC or NG is used, respectively. Generating a calibration curve using both NC and NG combined is not practicable, due to the infinite number of ratios between NC relative to NG or NG relative to NC that may be encountered during analysis. For this reason a calibration curve for the combined NC and NG was not performed. Instead the impact of NC with NG on the performance of the field method was evaluated from the results of the NC + NG test samples and compared to the respective STL reference method results for these samples.

Instrumentation and Materials

Colorimetric analyses were performed using a HACH DR/2010 spectrophotometer set in the absorbance mode at 507 nm. Samples were filtered into 25-mL glass cuvettes for the absorbance measurement. Other critical materials used in the analysis are listed below.

Zn dust:	Zinc, 325-mesh (Aldrich catalog # 20,998-8)
Ion exchange resin:	Alumin-A, 3-mL (Supelclean, Supelco 5-7082)
Filters:	0.45 µm syringe filters (Acrodisc, 25 mm)
Nitrite color development reagent:	NitriVer 3 powder pillow, 25-mL (Hach Company)

Method

An air-dried 20-gram aliquot of each sample (from each test group) was extracted by gently shaking 1.5 hours on an orbital shaker table with 100 mL of an acetone/3 percent water solution. The extraction time was determined by sampling an NG-spiked soil sample at 15 minute time intervals until a maximum response, 90 to 95 percent recovery, was achieved based on GC/TID analysis. After extraction, the sample was allowed to settle, and 20 mL of extract were

transferred to a 30mL syringe and filtered into a 20-mL amber VOA vial. These extracts were stored at 4°C pending analysis.

Prior to colorimetric development, the extracts were passed through a Supelco ion exchange resin to remove inorganic nitrites/nitrates. The extracts were then acidified with acetic acid and mixed with zinc dust. The reaction of the NG/NC with the acid and zinc dust removed nitro groups from the NC and NG analytes and generated inorganic nitrite ions, which were colorimetrically analyzed. The color was developed by adding the contents of a HACH NitriVer 3 powder pillow dissolved in deionized water to the zinc reacted solution. After 15 to 30 minutes, the color was developed, the sample was transferred to a 30mL syringe and filtered into a 25-mL cuvette and absorbance read at 507nm. A pink to rose color is indicative of the presence of NG/NC. This method was used to test each sample in each test group, for comparison to the reference NG- or NC- specific analysis performed.

Results

Calibration Sample Analyses

NC

The analysis results for the first eight NC samples (calibration samples) in each test group were used to create a calibration curve for NC. The curve was evaluated by testing six verification test samples spiked with intermediate concentrations of NC. Calibration curves were developed for each test group to determine the matrix influence on the analysis method. The measured CRREL response (absorbance) was graphed as a function of the spike concentration. In each case, the graphs for the four test groups were non-linear. Therefore, the concentrations were determined using a point to point calibration. The concentrations of NC in the NC test samples and in the NC and NG combined samples were calculated using the point to point calibration curves. The measured response for the sample containing 40,000 mg/kg NC was outside of the method range for the test groups and was not used in the calibration curve with the exception of the samples in the wood sample group, because the response was suppressed for these samples.

NG

A calibration curve was also generated using the first six NG-spiked samples (calibration samples) of each test group, and verified using the six test samples spiked with NG. Responses for NG were found to be linear and have absorbances 6 to 8 times higher than those for NC. The concentration of NG in the test samples and in the NC/NG combined samples were calculated using this curve.

For the STL reference methods 353.2 and 8330/8332 the results for the analysis of calibration samples were reported as absolute concentrations which were determined from the analysis of standard calibration solutions. The results of these analyses were compared to the known sample spike concentrations (in the method calibration spike samples to show the actual percent recovery for the method. The STL concentrations values were plotted against the known spike concentrations to determine a linear regression correlation between the reference method (STL 353.2 or STL 8330/8332) and the actual spike concentrations. The curve was used to correct the STL results to the calibration sample spike concentrations. The slope of this curve is the linear regression value for the STL method percent recovery for the sample set, and the regression R value is a measure of the data fit to the curve. The curve was used as the calibration curve to determine the NC or NG concentrations in the verification samples using results obtained from

STL. The results tables also show curve corrected results for the calibration samples, which when compared to the corresponding sample spike concentrations gives a point-by-point comparison of the results to the curve value. The percent difference between the two values (not shown) is a measurement of the fit for each data point.

For the CRREL analysis, a linear response to NG concentration was obtained. A linear regression calibration curve was prepared directly from the analytical response, measured at 507 nm absorbance, versus the spike concentrations of the calibration samples. The linear regression (R) value is a measure of the data fit to the curve. The curve was used to determine NG concentrations in the NG and the NC/NG combined verification/test samples. The results tables also show curve corrected results for the calibration samples, which when compared to the corresponding sample spike concentrations gives a point-by-point comparison of the results to the curve value. The percent difference between the two values (not shown) is a measure of the fit for each data point. The calibration data is shown in Tables 4-6 and 4-7. The curves are shown in Figures 4-14.

Verification/Test Sample Analyses

Results for the analyses of samples in each matrix were obtained using the corresponding method calibration curve described above. The results are reported in the tables as calibration curve corrected values in order to distinguish them from results obtained that are not calculated and reported using the curves generated from the calibration samples, such as STL's 353.2 and 8330/8332 reported results.

The percent difference between the calibration curve corrected values (sample results) and the spike concentrations have been calculated and tabulated along with the mean and standard deviation of the values. The percent difference was calculated by subtracting the spike concentration from the analysis result and dividing the difference by the spike concentration. Using this calculation a positive percent difference was indicative of a result biased high with respect to the spike concentration and a negative percent difference was indicative of a low biased result. This data provides a measurement of the agreement between the method results and spike concentration values in order to quantify method performance and aid in method comparisons. The mean percent difference is a measure of analytical accuracy by indicating the amount of bias in the data set values. Standard deviation is a measure of method precision for the data set.

In addition, a linear regression (R) value for each method was determined by plotting the sample results versus the spike concentrations. The linear regression (R) values for each data set are tabulated along with the standard deviation of the percent difference results. The linear regression value provides another measurement to determine the agreement between the sample results and the spike concentrations for the data set.

Results for each sample matrix are discussed separately below and presented in Table 4-6 for NG and NC calibration and test samples and Table 4-7 for the combined NC/NG test samples. Linear regression (R) results for analysis of the NG spiked test samples, NC-spiked test samples and combined NC/NG-spiked samples by the CRREL method are summarized in Tables 4-4 for NG results and Table 4-5 for NC results. Plots of calibration and test sample data are shown in Figures 4-14 and 4-15 in Appendix B.

Soil

NG

The detection limit for the analysis of NG in soil using the CRREL method was determined to be 5 mg/kg. Test results for the NG spiked test samples were consistent with the results obtained by STL using the 8330/8332 reference method. The standard deviations for the STL reference and CRREL methods were 10.2 percent and 11.2 percent, respectively. The mean of the percent difference results for the STL reference and the CRREL methods were both below 5 percent, which indicated a good correlation between the test results and the spike concentrations for both the STL reference and the CRREL methods.

The CRREL NG results for the combined NC- and NG-spiked soil samples as determined using the NG curve and compared to the NG spike concentrations only were found to be comparable to the reference method results. The mean percent difference (-19.2%) was slightly better than the mean of the percent differences for the STL 8330/8332 reference method (-30.1%) and the standard deviation of the percent difference was slightly higher (16.8%), but still within acceptable performance limits (±40%). Both methods indicated a negative or low bias with respect to the spike values. When the CRREL spike concentration was corrected for the nitrogen concentration contributed by the nitrocellulose in the samples the mean of the percent differences had a significantly greater negative bias (-78.5). The standard deviation for these results was 22.6 percent indicating reasonable precision.

NC

The detection limit for the CRREL analysis of soil samples spiked with NC was determined to be 50 mg/kg. The CRREL results for the NC spiked test samples were similar to the results using reference STL 353.2 method in that the standard deviation of the percent differences for both methods was high, 200 percent for the STL 353.2 method and 65.3 percent for the CRREL method. Both methods demonstrated a lack of precision for the analysis of NC on soil. The percent difference results for the reference method was most impacted by the result for the lowest spike concentration (10 mg/kg), which was biased high by 472 percent; the other results for the set were within 25 percent difference. The mean of the percent differences for the reference method was 126 percent, which indicates there is a significant positive bias to the results. The mean of the percent difference results for the CRREL method was -30.2, which indicated only a slightly negative bias for results determined using this method.

There was no correlation found between the NC CRREL results for the soils spiked with NC and NG, as determined with the NC curve and the reference method for analysis of NC. The mean of the percent differences for the CRREL method results calculated using the NC curve was 321 percent. The standard deviation of the percent differences was 417% indicating no correlation between analysis results and spiked concentrations. When the CRREL determined concentration was corrected for the nitrogen concentration contributed by the NG in the samples the mean of the percent differences was 255 percent and the standard deviation for these results was 352 percent indicating little improvement in the method using the NG (nitrogen) corrections. The mean of the percent differences for the combined NG and NC spiked soils as measured by the STL reference method (353.2) from the NC spike concentrations was 40.9 percent, which indicates a positive or high bias and was lower than the mean of the percent difference for the NC only spike samples (126%) using the same method of analysis. The standard deviation among the percent differences for the reference method was 27.5 percent, which was just outside the control limits for the method (20%). Better results were obtained for the STL reference

method for the combined NC and NG spike samples than what was obtained for the NC only spike samples.

Wallboard

NG

The detection limit for the CRREL analysis of wallboard samples spiked with NG was determined to be 5 mg/kg. Results of the NG spiked wallboard test samples were comparable with the results from reference STL 8330/8332 method and the GC-TID method. The standard deviation of the method percent differences, 17.2 percent, was similar to that for the other two comparison methods. The standard deviations for the STL 8330/8332 method and the GC-TID method were 16.9 percent and 9.1 percent, respectively. The mean of the method percent differences was 14.8 percent, which indicates there was no detectable bias to the results. The percent difference means for the other methods, -5.6 percent for the STL 8330/8332 method and -11.0 percent for the CRREL method, were similar and did not indicate any significant bias.

The ability to recover and quantify NG appears to be impeded by the presence of NC in the wallboard sample spike with both NC and NG. The mean of percent differences in the CRREL method using the NG curve was -30.0 percent, indicating a slight low bias. The standard deviation was 45.2 percent, which is above the recommended limit of 30 percent and is an indication of high variability between measurements. When the CRREL determined concentration was corrected for the NC contribution the mean of the percent differences from the corrected values indicated a large negative bias (-86.7), but with an acceptable precision or standard deviation of 5.7 percent. The results were comparable to those using the reference method (STL 8330/8332) with a similar negative bias with the mean of the percent differences of -59.0 percent and a standard deviation of 39.7 percent. The high negative bias (low results) and the high standard deviations make it difficult to relate results to the spike results in a predictable manner.

NC

The analysis of NC in both the reference method and the CRREL method showed high standard deviations. The standard deviation of percent differences was 54.1 percent, for the CRREL method and 519 percent for the reference method (STL 353.2). The mean of the method percent differences for the CRREL method was -7.3 percent, which indicates there was no detectable bias to the results. The mean of the percent differences for the STL 353.2 method was 284 percent indicating a strong positive bias in analysis results, especially at the lower concentrations.

Only two of the wallboard samples spiked with NC and NG could be quantitated using the CRREL method and the NC curve. The mean of the percent differences for results compared to the NC only spike concentrations was 130 percent and the analysis was highly variable, since the standard deviation for the percent differences was 210 percent. Results were similar when the CRREL results were compared to the NG (nitrogen) contribution spike concentrations; the mean of the percent differences was 94 percent and the standard deviation for the percent differences was 178 percent. The mean of the percent differences for the STL reference method was 67.5 percent indicating a high positive bias. The standard deviation of the percent differences for the reference method was 114 percent indicating high variability among measurements. Both the reference method and the CRREL method indicated an inability to accurately determine the concentration of NC in the wallboard matrix within the CRREL screening level recommended performance limits.

Wood

NG

The detection limit for the analysis of NG in wood using the CRREL method was determined to be 5 mg/kg. Test results for the NG spiked test samples were consistent with the results obtained by STL using the 8330/8332 reference method. The standard deviations for the STL reference and CRREL methods were 35.6 percent and 37.2 percent, respectively, indicating some variability in both methods. The means of the percent difference results for the STL reference and the CRREL methods were 9.0 and 29.5, respectively, indicating no significant bias in the reference, but possibly a slight positive bias in the CRREL method.

There was no apparent correlation between the CRREL NG results for the analysis of the NC and NG spiked wood samples and those for the reference method (STL 83308332). The mean of the percent differences when NG was determined using the NG curve and compared to the NG spike concentrations was 52.9 percent, and the standard deviation of the percent differences was 86.4 percent, which indicates a significant high bias and high variability among results. When the spike concentrations were corrected for NC (nitrogen) contribution the mean of the percent differences indicated a significant low bias (-62.3%), but lower variability (standard deviation of 30.7%). The reference method had no significant bias; the mean of the percent differences was -21.9 percent, and the standard deviation of the percent differences was 17.1 percent.

NC

NC could not be measured in spiked wood samples containing only NC at concentrations less than 4000 mg/kg using the CRREL method. Using the reference method, STL 353.3, NC could be quantitated at 50 mg/kg. The mean of the percent differences for the analysis of the NC spike wood samples using the reference method was 38.7 percent with a percent difference standard deviation of 33.9 percent, indicating a slightly positive bias and slightly high method variability.

It is believed that the wood matrix provided interference to the CRREL method chemistry that prevented a usable response for NC to be obtained. Since the method response for NC is much lower than that for NG, it is assumed that NC conversion to nitrite for analysis is incomplete for NC, and that matrix interferences can significantly affect the degree of conversion.

NC could not be measured in wood samples spiked with the combined NC and NG using the CRREL method. When NC was analyzed using the reference method the results were similar to those in the NC only spike wood samples. The mean of the percent differences was -21.9 percent, and the standard deviation of the percent differences was 17.1 percent, both within established control limits for the method on soil.

Cement

NG

NG could not be detected in any of the spike cement samples using the CRREL method. Results were similar to the results using the reference method (STL 8330) and the GC-TID method. (See discussion for NG results on cement for the EXPRAY™ and DROPEX^{PLUS} methods.)

For the combined NC and NG spiked samples the results were similar in that NG could not be evaluated because of the inability to recover meaningful concentrations of NG from the matrix for analysis.

NC

The detection limit for the CRREL method analysis of cement samples spiked with NC was determined to be 50 mg/kg. Results of the NC spike test samples were inconsistent with the results using reference STL 353.2 method; however, the standard deviation of the percent differences calculated for the CRREL method was 19.1 percent, which was an order of magnitude better than that for the reference method of 245 percent. The mean of the percent differences for the CRREL method was -9.3 indicating good correlation with the spike values while the percent difference results for the reference method was biased high by 206 percent. The STL 353.2 results were again most affected at the lower concentrations, i.e., below 80 mg/kg. At 2.5 and 10 mg/kg spike concentrations the STL 353.2 percent difference results were 551 percent and 377 percent, which were much higher than those for the 80 mg/kg and above spike concentrations that had percent differences from 2.9 percent to 79.0 percent.

NC analysis was found to be inconsistent for both the reference method and the CRREL method in the cement matrix when the samples were spiked with both NC and NG. The mean of the percent differences for the CRREL method using the NC curve results compared to the NC only spike concentrations was 266 percent. The mean of the percent differences when nitroglycerine (nitrogen) contribution was added to the spike concentrations was 138 percent. The standard deviations of the percent differences were both above 200 percent. Analysis using the STL reference method gave similar results. The mean of the percent differences was 109 percent, and the standard deviation was 66.3 percent, indicating a high positive bias and high variability.

Summary of CRREL Performance Parameters

The test sample CRREL analysis performance parameters are summarized below in Table 4-4 for NG and Table 4-5 for NC for the matrix test groups.

Table 4-4
Summary of CRREL Performance Parameters for NG Analysis

Matrix (Test Group)	Spike	Detection Limit (mg/kg)	Test Sample Analysis Performance Indicators		
			% Diff Mean	% Diff STD	LR R Value
Soil	NG	5	2.6	11.2	0.9991
	NG and NC	5	-19.2	16.8	0.9773
Wallboard	NG	5	14.8	17.2	0.9965
	NG and NC	25	-30.0	45.2	0.5611
Wood	NG	5	29.5	37.2	0.9937
	NG and NC	5	52.9	86.4	0.9549
Cement	NG	--	--	--	--
	NG and NC	--	--	--	--

The data provided in Table 4-4 should be used to define the method performance capabilities for the CRREL method for analysis of NG on samples of the matrices tested.

Table 4-5
Summary of CRREL Performance Parameters for NC Analysis

Matrix (Test Group)	Spike	Detection Limit (mg/kg)	Test Sample Analysis Performance Indicators		
			% Diff Mean	% Diff STD	LR R Value
Soil	NC	50	-30.2	65.3	0.9793
	NG and NC	--	321	417	0.3992
Wallboard	NC	50	-7.3	54.1	0.9977
	NG and NC	--	130	210	0.9660
Wood	NC	4000	--	--	--
	NG and NC	--	4179	--	--
Cement	NC	50	-9.3	19.1	0.9998
	NG and NC	--	266	279	--

The data provided in Table 4-5 should be used to define the method performance capabilities for the CRREL method for analysis of NC on samples of the matrices tested.

The CRREL method had a much lower response for NC as compared to NG, which elevated the detection limits for NC, and appeared to make the method susceptible to matrix interference in particular for the wood samples. It is most likely that the method chemistry does not provide complete conversion of the nitrogen (N) in NC to nitrite as it most likely does for NG and hence the large difference in response with the method for these two compounds. Since the conversion is incomplete, it would take little in the way of matrix interference to affect the degree of conversion and provide a detectable impact on method performance. This was most likely the reason for imprecise results for soil and wallboard samples as well.

Summary of MCAWW 353.2 Performance

The STL MCAWW353.2 method results were better for the analysis of NC on wood samples than the CRREL RDX method and this was attributed to matrix interference from the wood extract with the CRREL method. For the other matrices, however, the STL method results were mostly comparable to the CRREL results and correlated to spike concentrations, especially at concentrations of 80 mg/kg and above. At concentrations below 80 mg/kg there was a consistent high bias for the STL results, which can only be assumed to be due to matrix interference with the method at the lower concentrations. Even though the STL 353.2 reporting value was 2.0 mg/kg, the method results for matrix sample spikes were unreliable below 80 mg/kg and a practical quantitation limit at about 80 mg/kg for the method should be considered for these sample matrices.

Conclusion

- CRREL analysis of NG on wood, soil and wallboard samples was sensitive; a detection limit of 5 to 10 mg/kg, which is comparable to the reference method, was observed.

- The presence of NC with NG in the combined NC- and NG-spiked wallboard samples affected recovery and detection of NG. The results for NG were biased low by 30.0 percent. The detection limit for these samples was also increased to 25 mg/kg. This

same effect may have been observed with soil, but to a lesser degree as the mean percent difference of -19.2 percent indicated a smaller negative bias. These negative biases were also observed with the reference method and in similar magnitude, i.e., -30 percent for wallboard and -30.1 for soil.

- Analyses for NG only spiked soil samples were unbiased. The percent difference standard deviation (-19.2%) was better than the STL reference method (-30.1%). The percent difference standard deviation value of 37.2 percent; however, was not exceptional when compared to the 35.6 percent standard deviation value obtained for the reference method on wood samples.

- Analysis of NG on cement samples by CRREL could not be evaluated due to the low recovery of NG from the matrix, which was reproduced with similar results by other methods being evaluated, including the reference method (STL 353.2). It is believed that NG is not stable in the cement matrix.

- The analysis of NC in the wallboard matrix was inconsistent for the CRREL analysis. The CRREL analysis performed better than the reference method with means of percent of differences of 54.1 and 519 percent, respectively. It was determined that NC could not be effectively determined in wallboard containing both NC and NG combined. This was also the case with NC in the cement matrix were the mean of the percent difference was 9.3 for the CRREL method compared to 206 for the reference method, and the standard deviation was 19.1 for the CRREL method in comparison to 245 for the reference method.

- The analysis of NG using the CRREL method does not correlate well with the reference method (8330) results or the spike concentrations in wood samples when both NC and NG are present.

- NC could not be effectively analyzed in the wood matrix when present alone or when present in combination with NG.

- The STL 353.2 method results for the verification samples were consistently unreliable below about 80 mg/kg and a practical quantitation limit at about this concentration should be considered for samples of these matrices.

Table 4-6
CRREL Analysis Summary Site Soil - Nitroglycerine

SOIL			STL 8330				CRREL Method			GC-TID Method		
Calibration Samples	Matrix	Prepared Spike Concentration mg/kg	NG Reported Result mg/kg	Method % Recovery	NG Calibration Curve Corrected Value mg/kg		Abs at 507nm Reading	NG Calibration Curve Corrected Value mg/kg			NG Calibration Curve Corrected Value mg/kg	
BS-NG-SSB015	Soil	0	<0.50	--	--		0.011	0			ND	
BS-NG-SSB016	Soil	5	4.7	94%	8		0.053	3.60			2.7	
BS-NG-SSB017	Soil	20	20	100%	22		0.308	18.4			19.5	
BS-NG-SSB018	Soil	50	45	90%	46		0.895	52.6			43.6	
BS-NG-SSB019	Soil	100	96	96%	93		1.732	101			92.2	
BS-NG-SSB020	Soil	400	430	108%	402		6.876	400			417	

			STL 8330				CRREL Method			GC-TID Method		
Test Samples	Matrix	Prepared Spike Concentration mg/kg	NG Reported Result mg/kg		NG Calibration Curve Corrected Value mg/kg	Test Sample %Diff		NG Calibration Curve Corrected Value mg/kg	Test Sample %Diff		NG Calibration Curve Corrected Value mg/kg	Test Sample %Diff
BS-NG-SSB021	Soil	0	<0.5		--	--	0.014	--	--		ND	--
BS-NG-SSB022	Soil	2.5	2.1		--	--	0.013	--	--		ND	--
BS-NG-SSB023	Soil	10	8.5		12	17.3	0.131	8.13	-18.7		7.0	-30.0
BS-NG-SSB024	Soil	40	41		42	4.6	0.676	39.8	-0.05		44.5	11.3
BS-NG-SSB025	Soil	80	77		75	-6.0	1.472	86.1	7.6		76.3	-4.6
BS-NG-SSB026	Soil	250	260		245	-2.1	5.225	304	21.7		144	-42.4
					Mean	3.5		Mean	2.6		Mean	-16.44
					STD	10.2		STD	11.2		STD	24.2
					Linear Reg R	0.9993		Linear Reg R	0.9991		Linear Reg R	0.9419

Table 4-6
CRREL Analysis Summary Site Wallboard - Nitroglycerine

WALLBOARD			STL 8330				CRREL Method			GC-TID Method		
Calibration Samples	Matrix	Prepared Spike Concentration mg/kg	NG Reported Result mg/kg	Method % Recovery	NG Calibration Curve Corrected Value mg/kg		Abs at 507nm Reading	NG Calibration Curve Corrected Value mg/kg			NG Calibration Curve Corrected Value mg/kg	
BS-NG-WBB015	Wallboard	0	0	--	NC-UR		-0.001	4.6			ND	
BS-NG-WBB016	Wallboard	5	2.6	52%	7.0		0.014	6.2			5.2	
BS-NG-WBB017	Wallboard	20	10	50%	19		0.108	16.3			20.6	
BS-NG-WBB018	Wallboard	50	28	56%	48		0.406	48.4			58.3	
BS-NG-WBB019	Wallboard	100	58	58%	96		0.876	98.9			95	
BS-NG-WBB020	Wallboard	400	250	63%	401		3.686	401			400	

			STL 8330				CRREL Method			GC-TID Method		
Test Samples	Matrix	Prepared Spike Concentration mg/kg	NG Reported Result mg/kg		NG Calibration Curve Corrected Value mg/kg	Test Sample %Diff		NG Calibration Curve Corrected Value mg/kg	Test Sample %Diff		NG Calibration Curve Corrected Value mg/kg	Test Sample %Diff
BS-NG-WBB021	Wallboard	0	0		--	--	0.013	--			ND	--
BS-NG-WBB022	Wallboard	2.5	1.3		--	--	0.022	--			ND	--
BS-NG-WBB023	Wallboard	10	5.0		11	13.0	0.068	12.0	20.4		10.2	2.0
BS-NG-WBB024	Wallboard	40	22		38	-4.1	0.302	37.2	-7.0		32.8	-18.0
BS-NG-WBB025	Wallboard	80	34		57	-28.2	0.786	89.2	11.6		66.7	-16.6
BS-NG-WBB026	Wallboard	250	150		242	-3.1	3.075	335	34.2		222	-11.2
					Mean	-5.6		Mean	14.8		Mean	-11.0
					STD	16.9		STD	17.2		STD	9.1
					Linear Reg R	0.9905		Linear Reg R	0.9965		Linear Reg R	0.9993

Table 4-6
CRREL Analysis Summary Site Wood - Nitroglycerine

WOOD			STL 8330				CRREL Method			GC-TID Method		
Calibration Samples	Matrix	Prepared Spike Concentration mg/kg	NG Reported Result mg/kg	Method % Recovery	NG Calibration Curve Corrected Value mg/kg		Abs at 507nm Reading	NG Calibration Curve Corrected Value mg/kg			NG Calibration Curve Corrected Value mg/kg	
BS-NG-WDB015	Wood	0	<0.5	--			0.01	12.6			ND	
BS-NG-WDB016	Wood	5	11	220%	6		0.024	13.5			11.2	
BS-NG-WDB017	Wood	20	25	125%	21		0.11	18.8			24.0	
BS-NG-WDB018	Wood	50	54	108%	52		0.582	47.9			57.1	
BS-NG-WDB019	Wood	100	96	96%	97		1.041	76.3			93.7	
BS-NG-WDB020	Wood	400	380	95%	401		6.396	407			400	

			STL 8330				CRREL Method			GC-TID Method		
Test Samples	Matrix	Prepared Spike Concentration mg/kg	NG Reported Result mg/kg		NG Calibration Curve Corrected Value mg/kg	Test Sample %Diff		NG Calibration Curve Corrected Value mg/kg	Test Sample %Diff		NG Calibration Curve Corrected Value mg/kg	Test Sample %Diff
BS-NG-WDB021	Wood	0	<0.5		--	--	0.032	--	--		ND	--
BS-NG-WDB022	Wood	2.5	<0.5		--	--	0.032	--	--		ND	--
BS-NG-WDB023	Wood	10	19		14	41.6	0.057	15.5	55.2		10.2	2.0
BS-NG-WDB024	Wood	40	28		24	-40.5	0.293	30.1	-24.8		32.8	-18.0
BS-NG-WDB025	Wood	80	100		101	26.1	1.562	108	35.5		66.7	-16.6
BS-NG-WDB026	Wood	250	260		272	8.9	5.96	380	52.0		222	-11.2
					Mean	9.0		Mean	29.5		Mean	-11.0
					STD	35.6		STD	37.2		STD	9.1
					Linear Reg R	0.9865		Linear Reg R	0.9937		Linear Reg R	0.9993

Table 4-6
CRREL Analysis Summary Site Cement – Nitroglycerine

CEMENT			STL 8330				CRREL Method			GC-TID Method		
Calibration Samples	Matrix	Prepared Spike Concentration mg/kg	NG Reported Result mg/kg	Method % Recovery	NG Calibration Curve Corrected Value mg/kg	Method % Recovery	Abs at 507nm Reading	NG Calibration Curve Corrected Value mg/kg			NG Calibration Curve Corrected Value mg/kg	
BS-NG-CMB015	Cement	0	<0.5	--		--	0.003	--			ND	
BS-NG-CMB016	Cement	5	0.0	0.0%	0	0.0%	0.002	--			ND	
BS-NG-CMB017	Cement	20	0.087	0.4%	29	0.4%	0.003	--			ND	
BS-NG-CMB018	Cement	50	0.19	0.4%	63	0.4%	0.003	55.0			ND	
BS-NG-CMB019	Cement	100	0.24	0.2%	80	0.2%	0.008	80.0			ND	
BS-NG-CMB020	Cement	400	1.2	0.3%	400	0.3%	0.065	365			1.4[a]	

[a] value generated using soil curve

			STL 8330				CRREL Method			GC-TID Method		
Test Samples	Matrix	Prepared Spike Concentration mg/kg	NG Reported Result mg/kg	Test Sample %Diff			Abs at 507nm Reading	NG Calibration Curve Corrected Value mg/kg	Test Sample %Diff		NG Calibration Curve Corrected Value mg/kg	Test Sample %Diff
BS-NG-CMB021	Cement	0	<0.5	--			0.015	--	--		ND	--
BS-NG-CMB022	Cement	2.5	0.086	-96.6			0.016	--	--		ND	--
BS-NG-CMB023	Cement	10	0.45	-95.5			0.015	--	--		ND	--
BS-NG-CMB024	Cement	40	0.086	-99.8			0.015	--	--		ND	--
BS-NG-CMB025	Cement	80	0.25	-99.7			0.014	--	--		ND	--
BS-NG-CMB026	Cement	250	2.8	-98.9			0.033	--	--		0.72[a]	--
					Mean			Mean			Mean	--
					STD			STD			STD	--
					Linear Reg R			Linear Reg R			Linear Reg R	--

[a] value generated using soil curve

Table 4-6
CRREL Analysis Summary Site Soil – Nitrocellulose

SOIL			STL 353.20				CRREL Method		
Calibration Samples	Matrix	Prepared Spike Concentration mg/kg	NC Reported Result mg/kg	Method % Recovery	NC Calibration Curve Corrected Value mg/kg		Abs at 507nm Reading	NC Calibration Curve Corrected Value mg/kg	
BS-NC-SSB001	Soil	0	1.4 J B	--	--		0.000	--	
BS-NC-SSB002	Soil	5	2.8	56%	--		0.013	--	
BS-NC-SSB003	Soil	20	10.9	55%	69.5		0.007	--	
BS-NC-SSB004	Soil	50	28.9	58%	97.0		0.021	50	
BS-NC-SSB005	Soil	100	26.3	26%	93.0		0.056	100	
BS-NC-SSB006	Soil	400	125	31%	243		0.138	400	
BS-NC-SSB007	Soil	4000	2600	65%	4015		0.459	4000	
BS-NC-SSB008	Soil	40000	11200	28%	--		--	19477	

			STL 353.20				CRREL Method		
Test Samples	Matrix	Prepared Spike Concentration mg/kg	NC Reported Result mg/kg		NC Calibration Curve Corrected Value mg/kg	Test Sample %Diff	Abs at 507nm Reading	NC Calibration Curve Corrected Value mg/kg	Test Sample %Diff
BS-NC-SSB009	Soil	0	4.1		--	--	0.000	--	--
BS-NC-SSB010	Soil	2.5	3		--	--	0.007	--	--
BS-NC-SSB011	Soil	10	2.8		57.2	472	0.009	--	--
BS-NC-SSB012	Soil	80	24.1		89.6	12.1	0.040	77.9	-2.6
BS-NC-SSB013	Soil	250	170		312	24.8	0.148	512	-105
BS-NC-SSB014	Soil	2500	1530		2385	-4.6	0.288	2082	16.7
					Mean	126		Mean	-30.2
					STD	200		STD	65.3
					Linear Reg R	0.9995		Linear Reg R	0.9793

Table 4-6
CRREL Analysis Summary Site Wallboard – Nitrocellulose

WALLBOARD			STL 353.20				CRREL Method		
Calibration Samples	Matrix	Prepared Spike Concentration mg/kg	NC Reported Result mg/kg	Method % Recovery	NC Calibration Curve Corrected Value mg/kg	Test Sample %Diff	Abs at 507nm Reading	NC Calibration Curve Corrected Value mg/kg	
BS-NC-WBB001	Wallboard	0	27.3	--	--	--	0.000	--	
BS-NC-WBB002	Wallboard	5	2.6	52%	52.9	957	0.001	--	
BS-NC-WBB003	Wallboard	20	32.8	164%	119	494	0.014	20	
BS-NC-WBB004	Wallboard	50	1.8	4%	51.1	2.2	0.033	50	
BS-NC-WBB005	Wallboard	100	48.5	49%	153	53.2	0.046	100	
BS-NC-WBB006	Wallboard	400	135	34%	342	-14.4	0.151	400	
BS-NC-WBB007	Wallboard	4000	1810	45%	4004	0.1	0.286	4000	
BS-NC-WBB008	Wallboard	40000	14300	36%	31311	-21.7	--	--	

			STL 353.20				CRREL Method		
Test Samples	Matrix	Prepared Spike Concentration mg/kg	NC Reported Result mg/kg		NC Calibration Curve Corrected Value mg/kg	Test Sample %Diff	Abs at 507nm Reading	NC Calibration Curve Corrected Value mg/kg	Test Sample %Diff
BS-NC-WBB009	Wallboard	0	31.9		--	--	0.000	--	
BS-NC-WBB010	Wallboard	2.5	33		--	--	0.003	--	
BS-NC-WBB011	Wallboard	10	31.5		116	1061	0.006	--	
BS-NC-WBB012	Wallboard	80	43.5		142	77.9	0.018	26.3	-67.1
BS-NC-WBB013	Wallboard	250	107		281	12.4	0.132	346	38.4
BS-NC-WBB014	Wallboard	2500	957		2139	-14.4	0.236	2667	6.7
					Mean	284		Mean	-7.3
					STD	519		STD	54.1
					Linear Reg R	0.9998		Linear Reg R	0.9977

Table 4-6
CRREL Analysis Summary Site Wood - Nitrocellulose

WOOD			STL 353.20				CRREL Method		
Calibration Samples	Matrix	Prepared Spike Concentration mg/kg	NC Reported Result mg/kg	Method % Recovery	NC Calibration Curve Corrected Value mg/kg	Test Sample %Diff	Abs at 507nm Reading	NC Calibration Curve Corrected Value mg/kg	
BS-NC-WDB001	Wood	0	14.2	--	--	--	0.000	--	
BS-NC-WDB002	Wood	5	12.2	244%	--	--	0.000	--	
BS-NC-WDB003	Wood	20	15.5	78%	--	--	0.001	--	
BS-NC-WDB004	Wood	50	25.2	50%	105	111	0.003	--	
BS-NC-WDB005	Wood	100	31.7	32%	118	18.1	0.001	--	
BS-NC-WDB006	Wood	400	166	42%	380	-4.9	0.000	--	
BS-NC-WDB007	Wood	4000	2020	51%	4001	0.0	0.080	4000	
BS-NC-WDB008	Wood	40000	21100	53%	41267	3.2	0.209	40000	

			STL 353.20				CRREL Method		
Test Samples	Matrix	Prepared Spike Concentration mg/kg	NC Reported Result mg/kg		NC Calibration Curve Corrected Value mg/kg	Test Sample %Diff	Abs at 507nm Reading	NC Calibration Curve Corrected Value mg/kg	Test Sample %Diff
BS-NC-WDB009	Wood	0	14.2		--	--	0.000	--	--
BS-NC-WDB010	Wood	2.5	17.5		--	--	0.011	--	--
BS-NC-WDB011	Wood	10	16.2		--	--	0.006	--	--
BS-NC-WDB012	Wood	80	33.9		122	53.0	0.001	--	--
BS-NC-WDB013	Wood	250	180		408	63.1	0.002	--	--
BS-NC-WDB014	Wood	2500	1250		2498	-0.1	0.016	--	--
					Mean	38.7		Mean	--
					STD	33.9		STD	--
					Linear Reg R	0.9978		Linear Reg R	--

Table 4-6
CRREL Analysis Summary Site Cement - Nitrocellulose

CEMENT			STL 353.20				CRREL Method		
Calibration Samples	Matrix	Prepared Spike Concentration mg/kg	NC Reported Result mg/kg	Method % Recovery	NC Calibration Curve Corrected Value mg/kg	Test Sample %Diff	Abs at 507nm Reading	NC Calibration Curve Corrected Value mg/kg	
BS-NC-CMB001	Cement	0	2.7	--	--	--	0.000	--	
BS-NC-CMB002	Cement	5	6.2	124%	13	155.6	0.003	--	
BS-NC-CMB003	Cement	20	9.3	47%	19	-4.3	0.007	--	
BS-NC-CMB004	Cement	50	21.6	43%	44	-11.2	0.018	50	
BS-NC-CMB005	Cement	100	85.7	86%	176	76.0	0.049	100	
BS-NC-CMB006	Cement	400	256	64%	526	31.4	0.078	400	
BS-NC-CMB007	Cement	4000	1840	46%	3777	-5.6	0.368	4000	
BS-NC-CMB008	Cement	40000	19500	49%	40025	0.1	--	--	

			STL 353.20				CRREL Method		
Test Samples	Matrix	Prepared Spike Concentration mg/kg	NC Reported Result mg/kg		NC Calibration Curve Corrected Value mg/kg	Test Sample %Diff		NC Calibration Curve Corrected Value mg/kg	Test Sample %Diff
BS-NC-CMB009	Cement	0	3.6	--	--	--	0.000	--	--
BS-NC-CMB010	Cement	2.5	7.9	316%	16	551	0.002	--	--
BS-NC-CMB011	Cement	10	23.2	232%	48	377	0.003	--	--
BS-NC-CMB012	Cement	80	40.1	50%	82	2.9	0.024	59.7	-25.4
BS-NC-CMB013	Cement	250	218	87%	448	79.0	0.060	214	-14.4
BS-NC-CMB014	Cement	2500	1470	59%	3017	20.7	0.271	2796	11.8
					Mean	206		Mean	-9.3
					STD	245		STD	19.1
					Linear Reg R	0.9977		Linear Reg R	0.9998

Table 4-7
CRREL Summary - NG + NC Combined Spike

Soil	Prepared Spike Conc.				STL 8330			STL 353.2			CRREL - NG Curve Determined			CRREL - NC Curve Determined		
Sample Identification	NG (mg/Kg)	NC (mg/Kg)	N Based Total NC+NG as NG (mg/kg)	N Based Total NC+NG as NC (mg/kg)	NG Reported Value (mg/Kg)	NG Calibration Curve Corrected Value (mg/Kg)	Test Sample % Diff	NC Reported Value (mg/Kg)	NC Calibration Curve Corrected Value (mg/Kg)	Test Sample % Diff	NG Calibration Curve Corrected Value (mg/Kg)	Test Sample % Diff.	Test Sample % Diff. Based on Total Spike Conc.	NC Calibration Curve Corrected Value (mg/Kg)	Test Sample % Diff	Test Sample % Diff. Based on Total Spike Conc.
BS-CG-SSB027	0	0	0	0	0.13	4.0	--	14.3	74.7	--	1.16	--	--	0.0	--	--
BS-CG-SSB028	5.0	50	32.1	59.3	0.69	4.5	-10.0	32.5	102	89	3.60	-28.0	-88.8	80.9	61.8	36.5
BS-CG-SSB029	25	250	160	296	11.0	14.1	-43.8	198	355	35	20.6	-17.5	-87.1	2609	944	781
BS-CG-SSB030	100	1000	641	1185	63	62.2	-37.8	661	1060	5	69.7	-30.3	-89.1	2627	163	122
BS-CG-SSB030Dup	100	1000	641	1185	77	75.2	-24.8	966	1525	44	62.2	-37.8	-90.3	2157	116	82.0
BS-CG-SSB031	400	4000	2564	4740	280	263	-34.2	3570	5493	32	435	8.7	-83.0	--	--	--
BS-CG-SSB032	400	250	535	990	290	273	-31.9	320	541	29	360	-10.0	-32.8	--	--	--
						Mean	-30.1		Mean	40.9	Mean	-19.2	-78.5	Mean	321	255
						STD	11.8		STD	27.5	STD	16.8	22.6	STD	417	352
						Linear R	0.9982		Linear R	0.9929	Linear R	0.9773	--	Linear R	0.3992	--

Table 4-7
CRREL Summary - NG + NC Combined Spike

Wallboard	Prepared Spike Conc.				STL 8330			STL 353.2			CRREL - NG Curve Determined			CRREL - NC Curve Determined		
Sample Identification	NG (mg/Kg)	NC (mg/Kg)	N Based Total NC+NG as NG (mg/kg)	N Based Total NC+NG as NC (mg/kg)	NG Reported Value (mg/Kg)	NG Calibration Curve Corrected Value (mg/Kg)	Test Sample % Diff	NC Reported Value (mg/Kg)	NC Calibration Curve Corrected Value (mg/Kg)	Test Sample % Diff	NG Calibration Curve Corrected Value (mg/Kg)	Test Sample % Diff.	Test Sample % Diff. Based on Total Spike Conc.	NC Calibration Curve Corrected Value (mg/Kg)	Test Sample % Diff	Test Sample % Diff. Based on Total Spike Conc.
BS-CG-WBB027	0	0	0	0	0.21	3.7	--	52.1	161	--	6.7	--	--	0.0	--	--
BS-CG-WBB028	5.0	50	32.1	59.3	1.1	5.1	1.7	61.7	182	264	6.5	29.0	-79.9	0.0	--	--
BS-CG-WBB029	25	250	160	296	1.0	4.9	-80.3	103	272	8.9	15.5	-38.1	-90.3	203	-18.9	-31.5
BS-CG-WBB030	100	1000	641	1185	8.1	16.2	-83.8	463	1059	5.9	36.6	-63.4	-94.3	3787	279	220
BS-CG-WBB031	400	4000	2564	4740	150	242	-39.5	1640	3633	-9.2	409	2.2	-84.1	--	--	--
BS-CG-WBB032	400	250	535.25	990	15.0	27.2	-93.2	168	414	66	80.8	-79.8	-84.9	--	--	--
						Mean	-59.0		Mean	67.5	Mean	-30.0	-86.7	Mean	130	94
						STD	39.7		STD	113.8	STD	45.2	5.7	STD	210	178
						Linear R	0.4468		Linear R	0.9986	Linear R	0.5611	--	Linear R	0.9660	--

Table 4-7
CRREL Summary - NG + NC Combined Spike

Wood	Prepared Spike Conc.				STL 8330			STL 353.2			CRREL - NG Curve Determined			CRREL - NC Curve Determined		
Sample Identification	NG (mg/Kg)	NC (mg/Kg)	N Based Total NC+NG as NG (mg/kg)	N Based Total NC+NG as NC (mg/kg)	NG Reported Value (mg/Kg)	NG Calibration Curve Corrected Value (mg/Kg)	Test Sample % Diff	NC Reported Value (mg/Kg)	NC Calibration Curve Corrected Value (mg/Kg)	Test Sample % Diff	NG Calibration Curve Corrected Value (mg/Kg)	Test Sample % Diff.	Test Sample % Diff. Based on Total Spike Conc.	NC Calibration Curve Corrected Value (mg/Kg)	Test Sample % Diff	Test Sample % Diff. Based on Total Spike Conc.
BS-CG-WDB027	0	0	0	0	ND	--	--	6.9	69.7	--	14.2	--	--	0	--	--
BS-CG-WDB028	5.0	50	32.1	59.3	ND	--	--	23.1	101	103	14.3	185.7	-55.4	0	--	--
BS-CG-WDB029	25	250	160	296	28.0	23.8	-4.8	23.1	101	-59	18.6	-25.6	-88.4	0	--	--
BS-CG-WDB030	100	1000	641	1185	84	83.7	-16.3	330	701	-30	192	91.6	-70.1	42791	4179	3511
BS-CG-WDB031	400	4000	2564	4740	300	315	-21.3	17.1	89.6	-98	383	-4.3	-85.1	--	--	--
BS-CG-WDB032	400	250	535.25	990	210	219	-45.3	138	326	30	468	16.9	-12.7	--	--	--
						Mean	-21.9		Mean	-21.1	Mean	52.9	-62.3	Mean	4179	3511
						STD	17.1		STD	78.8	STD	86.4	30.7	STD	--	--
						Linear R	0.9089		Linear R	0.0035	Linear R	0.9549	--	Linear R	--	--

Table 4-7
CRREL Summary - NG + NC Combined Spike

Cement	Prepared Spike Conc.				STL 8330			STL 353.2			CRREL - NG Curve Determined			CRREL - NC Curve Determined		
Sample Identification	NG (mg/Kg)	NC (mg/Kg)	N Based Total NC+NG as NG (mg/kg)	N Based Total NC+NG as NC (mg/kg)	NG Reported Value (mg/Kg)	Test Sample % Diff	Test Sample % Diff	NC Reported Value (mg/Kg)	NC Calibration Curve Corrected Value (mg/Kg)	Test Sample % Diff	NG Calibration Curve Corrected Value (mg/Kg)	Test Sample % Diff.	Test Sample % Diff. Based on Total Spike Conc.	NC Calibration Curve Corrected Value (mg/Kg)	Test Sample % Diff	Test Sample % Diff. Based on Total Spike Conc.
BS-CG-CMB027	0	0	0	0	ND	--	--	3.9	8.06	--	--	--	--	0	--	--
BS-CG-CMB028	5.0	50	32.1	59.3	0.17	96.6	--	26.1	53.6	7.2	--	--	--	0.0	--	--
BS-CG-CMB029	25	250	160	296	0.23	99.1	--	260	534	113	--	--	--	276	10.3	-6.9
BS-CG-CMB030	100	1000	641	1185	2.3	97.7	--	1280	2627	163	--	--	--	1679	67.9	41.7
BS-CG-CMB031	400	4000	2564	4740	77	80.8	--	4920	10099	152	--	--	--	28331	608	498
BS-CG-CMB032	400	250	535.25	990	3.7	99.1	--	322	661	164	--	--	--	1194	378	20.7
					Mean	94.6			Mean	109				Mean	266	138
					STD	7.83			STD	66.3				STD	279	240
					Linear R	--			Linear R	--				Linear R	--	--

4.4 Quantitative Analysis for NG by GC/TID

Introduction

A field-capable GC instrument equipped with a TID was used to analyze the prepared sample extracts (of the NG test group and combined NC/NG test group) for NG. This method is selective for NG and does not produce a response for NC. The configuration is the same as the unit that is to be used in the proposed field demonstration. Following a simple extraction procedure, sample extracts are injected directly onto the GC column within a heated injection port. Analytical run times are typically less than 7 to 8 minutes.

This method is not applicable to the analysis of nitrocellulose because nitrocellulose is nonvolatile. In order for a compound to be analyzed by gas chromatography it needs to be volatilized into the gas phase. It is in the gas phase that the compound can be mobilized, transferred and separated in the column and subsequently transferred to the detector for analysis. In addition nitrocellulose decomposes at temperatures below the detector temperature and therefore is not detectable.

The first set of samples for each test group was used to determine the optimal working range of NG concentrations and develop a calibration curve. The remaining six were verification samples. The impact of NC + NG on the performance of the method was evaluated from the results of analysis of the six samples spiked with both NC + NG combined. A quadratic calibration curve was developed using the calibration samples for each test group. Results were calculated based on this curve. Instrument performance was continuously monitored by reanalysis of standards before and after each test group or every 10 samples.

Instrumentation

The GC used was the SRI Instruments (SRI) Model 8610C equipped with a heated TID, a heated on column injection port, and an internal air compressor. Separations were performed on a metal Crossbond 100 percent dimethyl polysiloxane column (DB-1), 15 m x 0.53 mm inside diameter, 0.5 micrometer film thickness.

The SRI Model 8610C is a transportable unit designed for field use Manual injections were made directly on the column using a 10 µL glass syringe with an extra long (6.0-7.0 cm) syringe needle that was supplied by SRI. GC data were collected on a Dell Latitude laptop computer using Peak Simple data collection software. The software was provided with the instrument from SRI.

Method

One 20-gram aliquot for each NG- and NG/NC-spiked sample was prepared for GC/TID analysis by extracting with acetone. This is the same extraction used in the colorimetric testing of EXPRAY™ and DROPEX^{PLUS} and is described in Section 4.2. Manual injections of 1 µL volumes of the acetone extracts were directly injected onto the GC using the following GC conditions, which were later optimized as described below.

Injection port temperature:	225°C
Detector temperature:	300°C
TID bead voltage:	-360 millivolts
Carrier, pressure:	N_2, 3 pounds per square inch (psi)
Internal air compressor pressure:	3 psi for make-up gas
GC oven temperature program:	95°C for 0.5 minutes
	20°C/min
	160°C for 2 minutes
	40°C/min
	240°C

These operating conditions yielded the greatest sensitivity (approximately 1.0 mg/L) and best resolution of NG. However, at these settings the method was unstable, requiring frequent recalibration. These conditions also appeared to contribute to premature bead failure, necessitating costly bead replacement and instrument downtime.

The SRI Model 8610C was returned to SRI to determine if the method instability resulted from the method settings or from defective hardware. The technicians at SRI concluded the instability was due to the instrument settings (high bead voltage and/or TID temperature). SRI developed a method with NG stability as the primary goal. Stability was improved, but sensitivity and resolution were sacrificed. The detection limit using this method was approximately 5.0 mg/L. Some loss of sensitivity occurred using this method, but sensitivity was regained by cutting approximately 5 inches off of the front of the column. The optimized operating conditions, which were used for the remainder of the study, were the following:

Injection port temperature:	180°C
Detector temperature:	250°C
TID bead voltage:	-300 millivolts
Internal air compressor pressure:	11 psi for the carrier gas
	2.0 psi for the make-up gas
GC oven temperature program:	120°C for 4.0 minutes
	15°C/min
	170°C for 4 minutes

Using the internal air compressor for both carrier and make-up gas eliminated the need for a high pressure gas cylinder, which is beneficial for field applications.

Further method development on instrument conditions should be performed to achieve better sensitivity and resolution but maintain method stability.

Results

Calibration Sample Analyses

A calibration curve for each sample matrix was generated from the first six samples (calibration samples) of each NG test group The GC/TID response curves as a function of spiked concentration for the four matrices were not linear, so a quadratic fit was used. The concentration for NG in the test samples and in the NC/NG combined test samples were calculated based on this curve. A calibration curve value for the calibration samples was also calculated based on this curve (calibration curve corrected value). For comparison purposes, the

results for the GC-TID analyses of the NG test group samples are summarized in Table 4-8 along with results for the lab reference method, STL (SW-846) Method 8330. The results for the GC/TID analysis of the combined NC and NG test group samples are summarized in Table 4-9. The STL 8330/8332 results are included for comparison, since it is a selective method for NG like the GC/TID method. The CRREL method is not selective for NG, since it yields a response for both NC and NG.

For the STL 8330/8332 analysis of calibration samples, results were reported from STL as absolute concentrations as determined from analyte standard solutions. These concentrations were compared to the calibration sample spike concentrations to show the actual percent recovery for the method. A linear regression plot was also made of the STL 8330/8332 results versus the spike concentrations to correct the STL results to the calibration sample spike concentrations. The slope of this curve is the linear regression value for the STL method percent recovery for the sample set, and the regression R value is a measure of the data fit to the curve. The curve was used as the calibration curve to determine NG concentrations in the verification samples using results obtained from STL. The results table also shows curve corrected results for the calibration samples, which, when compared to the corresponding sample spike concentrations, give a point-by-point comparison of the results to the curve value. The percent difference between the two values (not shown) is a measure of the fit for that data point.

For the CRREL analysis, a linear regression calibration curve was prepared directly from the analytical response, which was method absorbance at 507 nm, versus the spike concentrations of the calibration samples. The linear regression R value is a measure of the data fit to the curve. The curve was used to determine NG concentrations in the verification/test samples. The results table also shows curve corrected results for the calibration samples, which, when compared to the corresponding sample spike concentrations, give a point-by-point comparison of the results to the curve value. The percent difference between the two values (not shown) is a measure of the fit for that data point.

For the GC/TID analysis, analysis results of the calibration samples were used with the GC data software to generate a calibration curve. The curves were used to determine NG concentrations in the verification samples. The results table shows curve corrected results for the calibration samples, which, when compared to the corresponding sample spike concentrations, give a point-by-point comparison of the results to the curve value. The percent difference between the two values (not shown) is a measure of the fit for that data point.

Verification/Test Sample Analyses

Results for sample analyses for each matrix were obtained using the corresponding method calibration curve as described above and are reported in the tables as the calibration curve corrected values (to distinguish from results obtained that are not reported on the basis of the calibration samples, such as STL's 8330/8332 reported results).

The percent difference between the calibration curve corrected values (sample results) and the spike concentrations have been calculated and tabulated in the results tables along with the mean and standard deviation of the values. The percent difference was calculated by subtracting the spike concentration from the analysis result and dividing the difference by the spike concentration. Using this calculation a positive percent difference was indicative of a result biased high with respect to the spike concentration and a negative percent difference was indicative of a low biased result. These data provide a measure of the agreement between

method results and spike concentration values to quantify method performance and aid in method comparison. The mean percent difference measures analytical accuracy by indicating the amount of bias of results for the data set, and the standard deviation is a measure of method precision for the data set.

In addition, for each method a linear regression plot was generated of the sample results versus the spike concentrations. The linear regression R values for each data set are also tabulated in the results tables below the standard deviation of the percent difference results. This provides another measure of the agreement of sample results with spike concentration for the data set.

Results for each sample matrix are discussed separately below.

Soil

Soil results for analysis of the NG spiked test samples by GC-TID are shown in Table 4-8 and results for combined NC and NG spiked samples are shown in Table 4-9. Plots of calibration and test sample data are shown in Figures 4-16 and 4-17.

The detection limit for the GC/TID analysis of samples was 5 mg/kg. Results of the NG-spiked test samples were consistent with the results from the STL 8330/8332 reference method and the CRREL method. The standard deviation for the method percent differences was slightly higher at 24.2 percent but less than 25 percent. The percent differences for the STL reference and CRREL methods were 10.2 percent and 11.2 percent, respectively. The percent difference results for the GC-TID method were most impacted by the result for the highest spike concentration (250 mg/kg), which was low by 42 percent. The mean of the method percent differences was -16.4 percent, which indicates there was no detectable bias to the results. The mean of the percent difference results for the STL reference and the CRREL methods were both below 5 percent, which indicated a lack of bias for these methods as well.

For the combined NC- and NG- spiked samples, the standard deviation of the method percent differences was 17.6 percent, which was less than that for the NG only-spiked samples. The mean of the percent differences; however, was -27 percent, which indicates a negative bias, or generation of results that were biased low by 27 percent. This is a little higher than what is typically acceptable for a GC method, which is less than 25 percent, but within the ±40 percent performance limits for the CRREL field method. The STL 8330/8332 method showed a similar negative bias for these samples, with a mean of the percent differences of -30.4 percent. The standard deviation of the percent differences for the STL reference method was 11.8 percent.

Wallboard

Wallboard results for analysis of the NG spiked test samples by GC-TID are shown in Table 4-8 and results for NC and NG spiked samples are shown in Table 4-9. Plots of calibration and test sample data are shown in Figures 4-16 and 4-17.

The detection limit for the GC-TID analysis of NG-spiked samples was 5 mg/kg. The detection limit for the NG- and NC-spiked samples was higher at 25 mg/kg, as discussed below. Results of the NG-spiked test samples were comparable with the results from the STL 8330/8332 reference method and the CRREL method. The standard deviation of the method percent differences, 9.1 percent, was similar to that for the other two comparison methods. The standard deviations for the STL 8330/8332 method and the CRREL method were 16.9 percent and 17.2 percent, respectively. The mean of the method percent differences was -11 percent, which

indicates there was no detectable bias to the results. The percent difference means for the other methods, -5.6 percent for the STL 8330/8332 method and 14.8 percent for the CRREL method, also did not indicate any significant bias.

For the combined NC- and NG-spiked samples, it appears that the presence of NC impeded the ability to get complete recovery and quantification of NG based on the GC/TID results. The mean of the percent differences was -78.2 percent, which indicates a significant negative bias or generation of results that are biased low by 78.2 percent. Because of this, the detection limit was increased to 25 mg/kg for NG on wallboard with NC present. The standard deviation of the method percent differences; however, was seemingly not affected, because it was 15.1 percent, which was less than that for the NG only-spiked samples. This indicates the suppression effect was relatively consistent across the concentration range investigated. These results are comparable to those for the STL 8330/8332 reference method. A similar negative bias was observed, with a mean percent difference of -59.0 percent, i.e., results were low by an average of 59.0 percent. The standard deviation of the percent differences was 39.7 percent, which was significantly higher than that for the GC/TID method. The high negative bias and the high standard deviation for the percent differences for the STL reference method made it difficult to relate results to the spike concentrations in a predictable manner.

Wood

Wood results for analysis of the NG spiked test samples by GC-TID are shown in Table 4-8 and results for NC and NG spiked samples are shown in Table 4-9. Plots of calibration and test sample data are shown on Figures 4-16 and 4-17.

The detection limit for the GC/TID analysis of samples was 5 mg/kg NG. Results of the NG-spiked test samples were consistent with the results from the STL 8330/8332 reference method and the CRREL method. The standard deviation of the method percent differences, 9.1 percent, was significantly less than that for the other two methods. The standard deviations for the STL 8330/8332 method and the CRREL method were 35.6 percent and 37.2 percent, respectively. The mean of the method percent differences was 11 percent, which indicates there was no detectable bias to the results. The mean of the percent differences for the other methods was 9.0 percent for the STL 8330/8332 method and 29.5 percent for the CRREL method. While higher, the CRREL mean of the percent differences bias is not outside the method performance limits of ±40%.

For the combined NC- and NG-spiked samples, the standard deviation of the method percent differences was 6.3 percent, which was less than that for the NG only-spiked samples. The mean of the percent differences was -11.6 percent, which indicates a slight negative bias or generation of results that were biased low by 11.6 percent, which is within typical method performance limits. These results compare to the STL 8330/8332 reference method performance for the combined NC-and NG-spiked samples with a mean percent difference of -37.5 percent and a standard deviation of 37.9 percent. These results were most impacted by a nondetect result for the 5 mg/kg NG/50 mg/kg NC- spiked sample, but in general indicate a detectable negative bias.

Cement

Cement results for analysis of the NG spiked test samples by GC-TID are shown in Table 4-8 and results for NC and NG spiked samples are shown in Table 4-9. Plots of calibration and test sample data are shown on Figure 4-16.

A GC/TID peak response for NG was only detected on cement samples at 250 and 400 mg/kg. Due to the low response and limited data, an acceptable calibration curve could not be generated and sample analysis results could not be reported. Results were similar with both the STL 8330/8332 reference method and the CRREL method with less than 1 percent recovery of the actual spiked concentration. It is believed that NG may degrade by hydrolysis in the cement matrix due to the alkaline nature of the material. This is discussed in more detail in the description of EXPRAY™ and DROPEX^{PLUS} results in Section 4.2.

For the combined NC-and NG-spiked samples, the results were similar in that NG could not be evaluated because of the inability to recover meaningful concentrations of NG from the matrix for analysis.

Summary of GC/TID Performance Parameters

The test sample GC/TID analysis performance parameters are summarized below in Table 4-10 for the matrix test groups.

Table 4-10
Summary of GC-TID Performance Parameters for NG Analysis

Matrix (Test Group)	Spike	Detection Limit (mg/kg)	Test Sample Analysis Performance Indicators		
			% Diff Mean	% Diff STD	LR R Value
Soil	NG	5	-16.44	24.2	0.9419
	NG and NC	5	-27.2	17.6	0.9839
Wallboard	NG	5	-11.0	9.1	0.9993
	NG and NC	25	-78.2	15.1	0.5251
Wood	NG	5	-10.96	9.1	0.9993
	NG and NC	5	-11.6	6.3	0.9986
Cement	NG	--	--	--	--
	NG and NC	--	--	--	--

The data provided in Table 4-10 should be used to define the method performance capabilities for the GC-TID method for analysis of NG on samples of the matrices tested.

Conclusion

- Analysis of NG on cement samples by GC/TID could not be evaluated due to the low recovery of NG from the matrix, which was reproduced with similar results by other methods being evaluated, including the reference method (STL 8330/8332). It is believed that NG is not stable in the cement matrix.

- GC/TID analysis of NG on wood, soil, and wallboard samples was sensitive; a detection limit of 5 mg/kg, which is comparable to the reference method, was observed.

- The presence of NC with NG in the combined NC/NG-spiked wallboard samples impeded complete recovery and detection of NG. The results for NG were biased low by 78.2 percent. The detection limit for these samples was also increased to 25 mg/kg. This same effect may have been observed with soil, but to a lesser degree, as the mean percent difference of 27 percent indicated a smaller negative bias. These negative biases were

also observed with the reference method and in similar magnitude, i.e., -59 percent for wallboard and -30.4 for soil.

- Analyses for NG only-spiked soil samples were unbiased, but the percent difference standard deviation (24.2 percent) was higher than that for the STL reference method and the CRREL method at 10.2 and 11.2 percent, respectively. This was primarily due to a single result for the high concentration spiked sample that was low by 42.4 percent. The percent difference standard deviation value for all test methods was less than 25 percent, did not indicate any significant bias, and related predictably to the spike values.

- Wood and wallboard samples spiked with NG and wood samples spiked with NG and NC gave results with no significant bias and mean percent difference values of 12 percent or less.

- The GC/TID method gave noticeably superior results for the NG-spiked wood samples to the STL reference and the CRREL methods, which had percent difference standard deviations greater than 35 percent. For the combined NC- and NG-spiked samples, the STL reference method also gave results that were low by an average of 37.5 percent and in general did not relate predictably to the spike values.

Table 4-8
GC/TID Results for Site Soil - Nitroglycerine

SOIL			STL 8330				GC-TID Method		
Calibration Samples	Matrix	Prepared Spike Concentration mg/kg	NG Reported Result mg/kg	Method % Recovery	NG Calibration Curve Corrected Value mg/kg			NG Calibration Curve Corrected Value mg/kg	
BS-NG-SSB015	Soil	0	<0.50	--	--			ND	
BS-NG-SSB016	Soil	5	4.7	94%	8			2.7	
BS-NG-SSB017	Soil	20	20	100%	22			19.5	
BS-NG-SSB018	Soil	50	45	90%	46			43.6	
BS-NG-SSB019	Soil	100	96	96%	93			92.2	
BS-NG-SSB020	Soil	400	430	108%	402			417	

			STL 8330				GC-TID Method		
Test Samples	Matrix	Prepared Spike Concentration mg/kg	NG Reported Result mg/kg		NG Calibration Curve Corrected Value mg/kg	Test Sample %Diff		NG Calibration Curve Corrected Value mg/kg	Test Sample %Diff
BS-NG-SSB021	Soil	0	<0.5		--	--		ND	--
BS-NG-SSB022	Soil	2.5	2.1		--	--		ND	--
BS-NG-SSB023	Soil	10	8.5		12	17.3		7.0	30.0
BS-NG-SSB024	Soil	40	41		42	4.6		44.5	-11.3
BS-NG-SSB025	Soil	80	77		75	-6.0		76.3	4.6
BS-NG-SSB026	Soil	250	260		245	-2.1		144	42.4
					Mean	3.5		Mean	-16.44
					STD	10.2		STD	24.2
					Linear Reg R	0.9993		Linear Reg R	0.9419

Table 4-8. (continued) GC/TID Results for Site Wallboard – Nitroglycerine

WALLBOARD			STL 8330					GC-TID Method	
Calibration Samples	Matrix	Prepared Spike Concentration mg/kg	NG Reported Result mg/kg	Method % Recovery	NG Calibration Curve Corrected Value mg/kg			NG Calibration Curve Corrected Value mg/kg	
BS-NG-WBB015	Wallboard	0	0	--	NC-UR			ND	
BS-NG-WBB016	Wallboard	5	2.6	52%	7.0			5.2	
BS-NG-WBB017	Wallboard	20	10	50%	19			20.6	
BS-NG-WBB018	Wallboard	50	28	56%	48			58.3	
BS-NG-WBB019	Wallboard	100	58	58%	96			95	
BS-NG-WBB020	Wallboard	400	250	63%	401			400	

			STL 8330					GC-TID Method	
Test Samples	Matrix	Prepared Spike Concentration mg/kg	NG Reported Result mg/kg		NG Calibration Curve Corrected Value mg/kg	Test Sample %Diff		NG Calibration Curve Corrected Value mg/kg	Test Sample %Diff
BS-NG-WBB021	Wallboard	0	0		--	--		ND	--
BS-NG-WBB022	Wallboard	2.5	1.3		--	--		ND	--
BS-NG-WBB023	Wallboard	10	5.0		11	13.0		10.2	-2.0
BS-NG-WBB024	Wallboard	40	22		38	-4.1		32.8	18.0
BS-NG-WBB025	Wallboard	80	34		57	-28.2		66.7	16.6
BS-NG-WBB026	Wallboard	250	150		242	-3.1		222	11.2
					Mean	-5.6		Mean	-11.0
					STD	16.9		STD	9.1
					Linear Reg R	0.9905		Linear Reg R	0.9993

Table 4-8. (continued) GC/TID Results for Site Wood - Nitroglycerine

WOOD			STL 8330					GC-TID Method	
Calibration Samples	Matrix	Prepared Spike Concentration mg/kg	NG Reported Result mg/kg	Method % Recovery	NG Calibration Curve Corrected Value mg/kg			NG Calibration Curve Corrected Value mg/kg	
BS-NG-WDB015	Wood	0	<0.5	--				ND	
BS-NG-WDB016	Wood	5	11	220%	6			11.2	
BS-NG-WDB017	Wood	20	25	125%	21			24.0	
BS-NG-WDB018	Wood	50	54	108%	52			57.1	
BS-NG-WDB019	Wood	100	96	96%	97			93.7	
BS-NG-WDB020	Wood	400	380	95%	401			400	

			STL 8330					GC-TID Method	
Test Samples	Matrix	Prepared Spike Concentration mg/kg	NG Reported Result mg/kg		NG Calibration Curve Corrected Value mg/kg	Test Sample %Diff		NG Calibration Curve Corrected Value mg/kg	Test Sample %Diff
BS-NG-WDB021	Wood	0	<0.5		--	--		ND	--
BS-NG-WDB022	Wood	2.5	<0.5		--	--		ND	--
BS-NG-WDB023	Wood	10	19		14	41.6		10.2	-2.0
BS-NG-WDB024	Wood	40	28		24	-40.5		32.8	18.0
BS-NG-WDB025	Wood	80	100		101	26.1		66.7	16.6
BS-NG-WDB026	Wood	250	260		272	8.9		222	11.2
					Mean	9.0		Mean	-11.0
					STD	35.6		STD	9.1
					Linear Reg R	0.9865		Linear Reg R	0.9993

Table 4-8. (continued) GC/TID Results for Site Cement - Nitroglycerine

Cement			STL 8330				GC-TID Method		
Calibration Samples	Matrix	Prepared Spike Concentration mg/kg	NG Reported Result mg/kg	Method % Recovery	NG Calibration Curve Corrected Value mg/kg	Method % Recovery		NG Calibration Curve Corrected Value mg/kg	
BS-NG-CMB015	Cement	0	<0.5	--		--		ND	
BS-NG-CMB016	Cement	5	0.0	0.0%	0	0.0%		ND	
BS-NG-CMB017	Cement	20	0.087	0.4%	29	0.4%		ND	
BS-NG-CMB018	Cement	50	0.19	0.4%	63	0.4%		ND	
BS-NG-CMB019	Cement	100	0.24	0.2%	80	0.2%		ND	
BS-NG-CMB020	Cement	400	1.2	0.3%	400	0.3%		1.4 [a]	

[a] value generated using soil curve

			STL 8330				GC-TID Method		
Test Samples	Matrix	Prepared Spike Concentration mg/kg	NG Reported Result mg/kg		NG Calibration Curve Corrected Value mg/kg	Test Sample %Diff		NG Calibration Curve Corrected Value mg/kg	Test Sample %Diff
BS-NG-CMB021	Cement	0	<0.5			--		ND	--
BS-NG-CMB022	Cement	2.5	0.086		28	1035		ND	--
BS-NG-CMB023	Cement	10	0.45		150	1397		ND	--
BS-NG-CMB024	Cement	40	0.086		28	-29.1		ND	--
BS-NG-CMB025	Cement	80	0		0	-100		ND	--
BS-NG-CMB026	Cement	250	2.8		933	273		0.72 [a]	--
					Mean	515		Mean	--
					STD	667		STD	--
					Linear Reg R	0.8432		Linear Reg R	--

Table 4-9
GC-TID Results for Site Soil - NG+NC Spiked

Sample Identification	Matrix	Prepared Spike Conc.		STL 8330			GC/TID	
		NG (mg/Kg)	NC (mg/Kg)	NG Reported Value (mg/Kg)	NG Calibration Curve Corrected Value (mg/Kg)	Test Sample % Diff	NG Calibration Curve Corrected Value (mg/Kg)	Test Sample % Diff
BS-CG-SSB027	Soil	0	0	0.13	4.0	--	ND	--
BS-CG-SSB028	Soil	5	50	0.69	4.5	10.0	3.18	36.4
BS-CG-SSB029	Soil	25	250	11	14.1	43.8	13.6	45.6
BS-CG-SSB030	Soil	100	1000	63	62.2	37.8	55.4	44.6
BS-CG-SSB030 Dup	Soil	100	1000	77	75.2	24.8	81.9	18.1
BS-CG-SSB031	Soil	400	4000	280	263	34.2	391	2.3
BS-CG-SSB032	Soil	400	250	290	273	31.9	334	16.5
					Mean	-30.4	Mean	-27.2
					STD	11.8	STD	17.6
					Linear R	0.9982	Linear R	0.9839

Table 4-9. (continued)
GC-TID Results for Site Wallboard - NG+NC Spiked

Sample Identification	Matrix	Prepared Spike Conc.		STL 8330			GC/TID	
		NG (mg/Kg)	NC (mg/Kg)	NG Reported Value (mg/Kg)	NG Calibration Curve Corrected Value (mg/Kg)	Test Sample % Diff	NG Calibration Curve Corrected Value (mg/Kg)	Test Sample % Diff
BS-CG-WBB027	Wallboard	0	0	0.21	3.7	--	ND	--
BS-CG-WBB028	Wallboard	5	50	1.1	5.1	-1.7	ND	--
BS-CG-WBB029	Wallboard	25	250	1.0	4.9	80.3	4.4	82.4
BS-CG-WBB030	Wallboard	100	1000	8.1	16.2	83.8	15	85.0
BS-CG-WBB031	Wallboard	400	4000	150	242	39.5	176	56.0
BS-CG-WBB032	Wallboard	400	250	15.0	27.2	93.2	42.6	89.4
					Mean	-59.0	Mean	-78.2
					STD	39.7	STD	15.1
					Linear R	0.4468	Linear R	0.5251

Table 4-9. (continued)
GC-TID Results for Site Wood - NG+NC Spiked

Sample Identification	Matrix	Prepared Spike Conc.		STL 8330			GC/TID	
		NG (mg/Kg)	NC (mg/Kg)	NG Reported Value (mg/Kg)	NG Calibration Curve Corrected Value (mg/Kg)	Test Sample % Diff	NG Calibration Curve Corrected Value (mg/Kg)	Test Sample % Diff
BS-CG-WDB027	Wood	0	0	ND	--	--	ND	--
BS-CG-WDB028	Wood	5	50	ND	--	100	ND	--
BS-CG-WDB029	Wood	25	250	28	23.8	4.8	21.6	13.6
BS-CG-WDB030	Wood	100	1000	84	83.7	16.3	97.8	2.2
BS-CG-WDB031	Wood	400	4000	300	315	21.3	342	14.5
BS-CG-WDB032	Wood	400	250	210	219	45.3	336	16.0
					Mean	-37.5	Mean	-11.6
					STD	37.9	STD	6.3
					Linear R	0.9089	Linear R	0.9986

Table 4-9. (continued)
GC-TID Results for Site Cement - NG+NC Spiked

Sample Identification	Matrix	Prepared Spike Conc.		STL 8330			GC/TID	
		NG (mg/Kg)	NC (mg/Kg)	NG Reported Value (mg/Kg)	Test Sample % Diff	Test Sample % Diff	NG Calibration Curve Corrected Value (mg/Kg)	Test Sample % Diff
BS-CG-CMB027	Cement	0	0	ND		--	ND	--
BS-CG-CMB028	Cement	5	50	0.17	96.6	--	ND	--
BS-CG-CMB029	Cement	25	250	0.23	99.1	--	ND	--
BS-CG-CMB030	Cement	100	1000	2.3	97.7	--	ND	--
BS-CG-CMB031	Cement	400	4000	77	80.8	--	--	--
BS-CG-CMB032	Cement	400	250	3.7	99.1	--	--	--
				Mean	94.6	--	Mean	--
				STD	7.8	--	STD	--
							Linear R	--

5.0 SUMMARY OF CONCLUSIONS

The specific goals of the study are listed below along with a summary of accomplishment for each.

1) Verify that usable calibration data may be obtained for BAAAP NC analysis using the CRREL RDX method and the MCAWW 353.2 Method – Calibration curves for analysis of NC using the methods were prepared and were usable. The calibration curves using the MCAWW 353.2 method were linear with good correlation to spike concentrations. The calibration curves using the CRREL RDX method were non-linear, but did correlate in a predictable manner to concentrations, such that point-to-point curves could be used to obtain results from sample analyses.

2) Compare the qualitative screening indications from EXPRAY™ / DROPEX^{PLUS} and Raman screening methods to the quantitative results for NC analysis using MCAWW 353.2 for NC – These comparisons were performed and are described in the EXPRAY™/ DROPEX^{PLUS} and Raman method sections.

3) Compare the qualitative screening indications from EXPRAY™ and Raman screening with the quantitative analytical results for NG using SW-846 Method 8332 and GC/TID - These comparisons were performed and are described in the EXPRAY™/ DROPEX^{PLUS} and Raman method sections.

4) Compare the quantitative analytical results between the ESTCP demonstration methods for NG detection (CRREL RDX method, EPA Method 8330/8332, and GC/TID) - These comparisons were performed and are described in the CRREL RDX and GC/TID method sections.

5) Compare the quantitative results between the demonstration methods for NC (CRREL RDX Method and MCAWW 353.2) - These comparisons were performed and are described in the CRREL RDX method sections.

6) Determine the effect of NC and NG mixtures in the same sample on the quantitative results obtained from the non-specific methods and compound-specific methods - These comparisons were performed and are described in the sections for each method.

5.1 Cement Matrix Interference with NG Analyses

NG spike concentrations were not stable in the cement matrix. In many cases in only the highest concentration NG spiked samples was NG detected. This was confirmed with all NG methods, EXPRAY™, DROPEX^{PLUS}, CRREL RDX and STL SW-846 8330/8332.

5.2 Raman Spectroscopy

Raman spectroscopy was not useful for the analysis of the bulk sample matrices for the presence of NC at concentrations up to 40,000 mg/kg or for the presence of NG at concentrations up to 400 mg/kg. The only detection occurred with the 4 percent NC spiked wood sample when the laser was focused directly on a visible NC deposit at a distance of 0.5 cm using the videoscope to assist targeting. Darker sample matrices may absorb enough of the Raman excitation laser

energy to be burned or charred during analysis and it is possible that energetic material in close proximity may be ignited.

5.3 DROPEX^{PLUS} / EXPRAY™

Both test kits seemed to work equally well and correlate well with the reference method, STL 8330/8332, with limitations based on detectable concentration limits for each matrix, which were matrix dependent. Except for three test results, sample concentrations above the method's detectable limit were all positive. The three false negative results were for sample concentrations near but just above the detectable limit. As noted above, the test responses were faint for concentrations near the detectable limit, so a false negative near the limit can result from a slight variation in test conditions or performance. Of the three false negative results, one was with EXPRAY™ and two were with DROPEX^{PLUS}. For sample concentrations below the detectable limit all results were negative. These could be considered false negatives (except for unspiked background samples), if the detectable limit is not realized. All unspiked background matrix samples gave negative results, so there were no false positives.

The DROPEX^{PLUS} test had lower detectable limits for NC on three of the four sample matrices; soil, wallboard and wood. NG EXPRAY™ had a lower detectable limit for wallboard while DROPEX^{PLUS} had a lower detectable limit for wood. For the combined NC and NG spiked samples the DROPEX^{PLUS} test had lower detectable limits on two of the four sample matrices; wood and cement. DROPEX^{PLUS} also showed a slightly better response than EXPRAY™ when tested at 4° C.

5.4 CRREL RDX Method

The wood matrix gave some yellow color interference for the method, which is a colorimetric method, and produced low responses for NC. A response for wood was only obtained at the 4000 and 40,000 mg/kg concentration. The results for NG on wood trended consistent with spike concentrations, but with a high degree of variability. Method specific conclusions are summarized below.

- CRREL analysis of NG on soil and wallboard samples was sensitive; a detection limit of 5 to 10 mg/kg, which is comparable to the reference method, was observed.

- The presence of NC with NG in the combined NC and NG spiked wallboard samples affected recovery and detection of NG. The results for NG were biased low by 30.0 percent. The detection limit for these samples was also increased to 25 mg/kg. This same effect may have been observed with soil, but to a lesser degree as the mean percent difference of -19.2 percent indicated a smaller negative bias. These negative biases were also observed with the reference method and in similar magnitude, i.e., -30 percent for wallboard and -30.1 for soil.

- Analyses for NG only spiked soil samples were unbiased. The percent difference standard deviation (-19.2%) was better than the STL reference method (-30.1%). The percent difference standard deviation value of 37.2 percent; however, was not exceptional when compared to the 35.6 percent standard deviation value obtained for the reference method on wood samples.

- Analysis of NG on cement samples by CRREL could not be evaluated due to the low recovery of NG from the matrix, which was reproduced with similar results by other methods being evaluated, including the reference method (STL 353.2). It is believed that NG is not stable in the cement matrix.

- The analysis of NC in the wallboard matrix was inconsistent for the CRREL analysis. The CRREL analysis performed better than the reference method with means of percent of differences of 54.1 and 519 percent, respectively. It was determined that NC could not be effectively determined in wallboard containing both NC and NG combined. This was also the case with NC in the cement matrix where the mean of the percent difference was 9.3 for the CRREL method compared to 206 for the reference method, and the standard deviation was 19.1 for the CRREL method in comparison to 245 for the reference method.

- The analysis of NG using the CRREL method does not correlate well with the reference method (8330) results or the spike concentrations in wood samples when both NC and NG are present.

- Nitrocellulose could not be effectively analyzed in the wood matrix using the CRREL method when present alone or when present in combination with NG. In general, the analysis of NC by the CRREL method was imprecise and this was attributed to the low response for NC compared to NG. It is assumed that the conversion of NC to nitrite for analysis is not complete for NC and that matrix interferences could easily affect the degree of conversion and impact the method precision.

- Comparison of the CRREL method performance to the MCAWW 353.2 reference method was hampered by a consistent high bias for the MCAWW 353.2 method results for sample spikes at concentrations of about 80 mg/kg and below. This was attributed to matrix interference with 353.2 method performance at the low concentrations.

5.5 GC/TID Method

The GC/TID results for NG on soil, wallboard, and wood were in general found to be consistent with spike concentrations. Response correlations to spike concentrations were acceptable. Results were good with detection limits of 5 mg/kg with. NG was only just detectable at the highest concentrations (250-400 mg/kg) on cement matrix; however, the reference method 8330/8332 performance was equally poor for this matrix.

For the field demonstration optimization of the 5 mg/kg detection limit, without sacrificing response stability or causing bead failure necessitating costly bead replacement and instrument downtime, would be beneficial. A level of detection below the established site clean-up criteria of 3.6 mg/kg NG may be achievable with additional optimization of operating parameters.

Specific matrix dependent findings are detailed below:

- Analysis of NG on cement samples by GC/TID could not be evaluated due to the low recovery of NG from the matrix, which was reproduced with similar results by other methods being evaluated, including the reference method (STL 8330/8332). It is believed that NG is not stable in the cement matrix.

- GC/TID analysis of NG on wood, soil and wallboard samples was sensitive; a detection limit of 5 mg/kg, which is comparable to the reference method, was observed.

- The presence of NC with NG in the combined NC/NG spiked wallboard samples impeded complete recovery and detection of NG. The results for NG were biased low by 78.2 percent. The detection limit for these samples was also increased to 25 mg/kg. This same effect may have been observed with soil, but to a lesser degree as the mean percent difference of 27.2 percent indicated a smaller negative bias. These negative biases were also observed with the reference method and in similar magnitude, i.e., -59.0 percent for wallboard and -30.4 for soil.

- Analyses for NG only spiked soil samples were unbiased but the percent difference standard deviation (24.2%) was higher than that for the STL reference method and the CRREL method at 10.2 and 11.2 percent respectively. This was primarily due to a single result for the high concentration spiked sample that was low by 42.4 percent. The percent difference standard deviation value for all test methods was less than 25 percent and did not indicate any significant bias and related predictably to the spike values.

- Wood and wallboard samples spiked with NG and wood samples spiked with NG and NC gave results with no significant bias and mean percent difference values of 12 percent or less.

- The GC/TID method gave noticeably superior results for the NG spiked wood samples to the STL reference and the CRREL methods, which had percent difference standard deviations greater than 35 percent. For the combined NC and NG spiked samples the STL reference method also gave results that were low by an average of 37.5 percent, and in general did not relate predictably to the spike values.

6.0 Impact to Field Demonstration

Bench scale testing determined that Raman spectroscopy was not useful for the analysis of the bulk sample matrices for the presence of NC at concentrations up to 40,000 mg/kg or for the presence of NG at concentrations up to 400 mg/kg. The only detection occurred with the 4 percent NC spiked wood sample when the laser was focused directly on a visible NC deposit at a distance of 0.5 cm using the videoscope to assist targeting. Darker sample matrices may absorb enough of the Raman excitation laser energy to be burned or charred during analysis and it is possible that energetic material in close proximity may be ignited. Due to these factors it is recommended Raman spectroscopy not be used during the field demonstration.

For the field demonstration optimization of the 5 mg/kg detection limit, without sacrificing response stability or causing bead failure necessitating costly bead replacement and instrument downtime, would be beneficial. A level of detection below the established site clean-up criteria of 3.6 mg/kg NG may be achievable with additional optimization of operating parameters. Optimization of GC/TID operating parameters should be investigated prior to the field investigation. Improved sensitivity and chromatography may be obtained by monitoring performance and responding to early signs of degradation by clipping the front end of the column, which can become fouled.

The CRREL RDX method response for NC was 8-10 times lower than the response for NG for all four matrices tested. Additional testing is needed to possibly optimize the method detectable levels for NC detection in the field demonstration. A single extraction with a lower solvent to material ratio would also be beneficial (per the method a 5:1 ratio was used for the bench scale test). This single extract could be used for all the field methods and would reduce the sample size requirement, analysis steps and potentially provide a benefit to method sensitivity.

Because of the poor performance for the MCAWW 353.2 method for analysis of NC concentrations below 80 mg/kg for the matrix verification samples, a practical quantitation limit higher than the lab reporting limit should be considered for application to sample analysis results.

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APPENDIX A
SAMPLE SPIKING PROCEDURE FOR NITROCELLULOSE

PROCEDURE FOR NITROCELLULOSE

SPIKE SAMPLE PREPARATION

EQUIPMENT AND MATERIALS:

1. Analytical balance.
2. 1 - Wide mouth bottle – high density polypropylene (Nalgene), 125 milliliter (mL)
3. Volumetric flask – 1 liter
4. 4 oz. and 8 oz wide mouth soil sample jars with Teflon lined lids
5. 2 - Amber bottles – 1 liter
6. 1 - Small glass bowl
7. 2 – small stainless steel spatulas
8. 3 liters nitrite-free distilled water
9. Acetone – commercial grade acceptable
10. Blender – 1.5 liter capacity with glass cup and blades
11. Sonicator with small probe
12. 1 – high-density polypropylene wash bottle, 500 mL
13. 2 - Glass pipettes, 10 mL, with 0.1 mL divisions
14. 1 – glass graduated cylinder, 100 mL
15. Approximately 4000 grams (dry) of clean soil, wallboard, wood and cement. Material should be a composite of typical site sample types found at site. Composited material should be well graded with some fines and no organic material.
16. Approximately 4000 grams dry crushed concrete (spalled or chipped from BAAAP building floor)
17. Approximately 4000 grams dry crushed wallboard material from clean BAAAP production building.
18. Approximately 4000 grams finely shaved or chipped wood from a structural member of a clean BAAAP building.
19. Dry, clean nitrocellulose (NC) from BAAAP production process or of similar composition (TAL reference material: 71% flake NC with isopropyl alcohol, RS ½ sec, lot 9H-9027, Hercules, Inc.). Obtain the following weighed quantities:

1 – 2.0 grams	+/- 0.005g
4 – 1.6 grams	+/- 0.004g
4 – 0.16 grams	+/- 0.004g
4 – 40 milligrams	+/- 2 milligrams (mg)

PROCEDURE

Preparation

1. Dry the soil, concrete, wood, and wallboard bulk samples.
2. Screen each bulk sample with No. 4 sieve. Break up clumps if necessary.
3. Prepare samples of each matrix as follows:
   14 samples of 20 grams each (x 3)
   12 samples of 20 grams each (x 3)
   6 samples of 20 grams each (x 3)

Measure each sample into a wide mouth jar. Weigh each to +/- 0.1 gram.

4. Label jars according to the Field Sampling Plan. The six samples of 20 grams (x 3) for NC/NG combined spike for each matrix are to be labeled and set aside for future use.

Sample Spiking for 4,000 and 40,000 milligrams/kilogram (mg/kg) Calibration samples and 2000 mg/kg Method Verification sample

1. Place correct weighed portions of NC into the proper jars according to Tables 1 and 2.
2. Measure 5 mL of nitrate-free water into each jar.
3. Place lid on jars and shake vigorously for 2 minutes.

Concentrated NC suspension Preparation (2000mg/Liter) for 500, 100 mg/kg samples

1. Place 2 grams dry NC in blender cup.
2. Measured 1000 mL of nitrite-fee water using volumetric flask. With the blender off, add ½ of the water to the blender contents.
3. Allow the NC to become thoroughly wetted. Use a stir rod to break up clumps if necessary.
4. Cover blender.
5. Bring blender up to lowest speed as gently as possible to avoid adding air. Blend on low speed for 5 minutes.
6. Carefully transfer blender contents using remaining 0.5 liters of water to a clean 1 liter amber jar. Using magnetic stir plate, continuously stir on slowest speed for continuous mixing (to maintain suspension). Label and store in cool, dark location
7. Carefully measure required amount of concentrated suspension into correct jars (see Calibration Sample Preparation Table 1 and Method Verification Sample Preparation Table 2). .
8. Place cap on jars and shake vigorously for 2 minutes.

Dilute NC Suspension Preparation (200mg/Liter) for 50, 20, 5 mg/kg samples

1. Measure 900 mL of nitrate-free water into volumetric flask (fill flask to line, remove and discard 100 mL using graduated cylinder).
2. Fill wash bottle with part of measured water.
3. Quickly measure 100 mL of the concentrated suspension into a 2nd 1 liter amber bottle using graduated cylinder. Rinse the graduated cylinder into the bottle with wash bottle.
4. Clean out blender with acetone and rinse with stock nitrate-free water (not from the measured quantity).
5. Pour remainder of measured 900 mL of nitrite-free water into jar rinsing wash bottle contents into jar.
6. Cover jar and continuously stir on magnetic stirrer using slow speed
7. Using fresh 10 mL pipette, transfer the amount of the diluted suspension to the appropriate sample jars according to Table A-1 and Table A-2.
8. Place lids on all samples and seal. Shake each sample jar vigorously for 2 minutes.

Blank Preparation

1. Use fresh 10 mL pipette and add 5 mL of pure nitrate free water from stock to each of the sample blanks.

2. Place lids on all samples and seal. Shake each sample jar vigorously for 2 minutes.

Hold the samples prepared for combined NC/NG spiking until the results of the bench scale study using NC- and NG-spiked samples are complete. They will be spiked with varying combined concentrations of NC and NG. The concentrations will be determined according to the best working ranges for the analytical methods of the study.

Table A-1
Suspension Volumes For
Nitrocellulose Calibration Spiked Samples

Calibration NC Concentration (Mg/Kg)	Grams Dry NC to add to each 20 Grams Sample	Notes
40000	0.8	
4000	0.08	
	Ml Concentrated Suspension to add to each 20 Grams Sample	
500	5	
100	1	
	Ml Diluted Suspension to add to each 20 Grams Sample	
50	5	
20	2	
5	0.5	
0	0	Blank (5 mL Nitrate Free Water added to Soil)

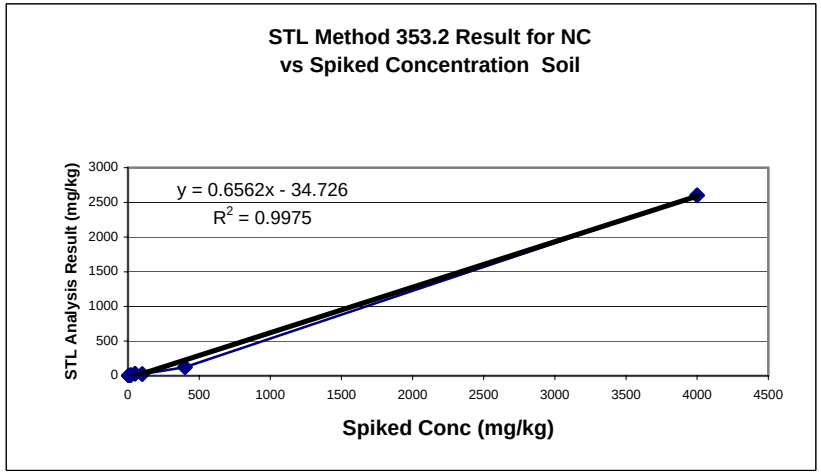
Table A-2
Suspension Volumes for
Nitrocellulose Method Verification Spiked Samples

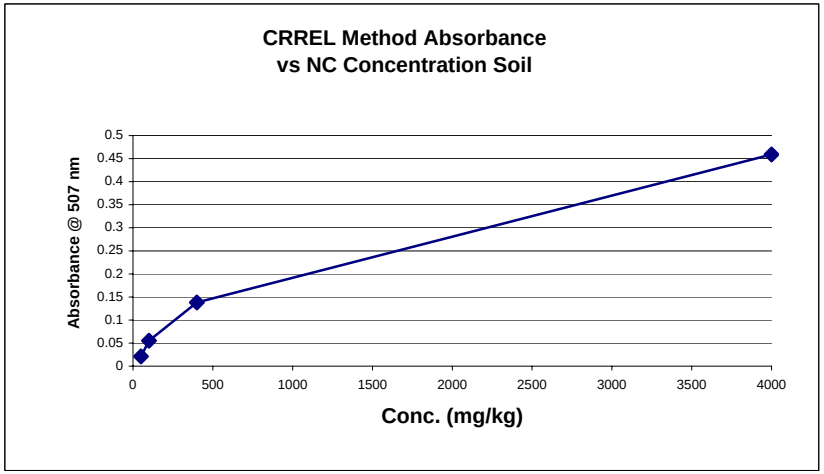
Calibration NC Concentration (Mg/Kg)	Grams Dry NC to add to each 20 Grams Sample	Notes
2000	0.04	
	Ml Concentrated Suspension to each add 20 Gram Sample	
200	2	
	Ml Diluted Suspension To Add To Each 20 Grams Sample	
80	8	
10	1	
2	0.2	
0	0	Blank (5 mL Nitrate Free Water Added To Soil)

APPENDIX B
CALIBRATION CURVE PLOTS AND TEST SAMPLE GRAPHS

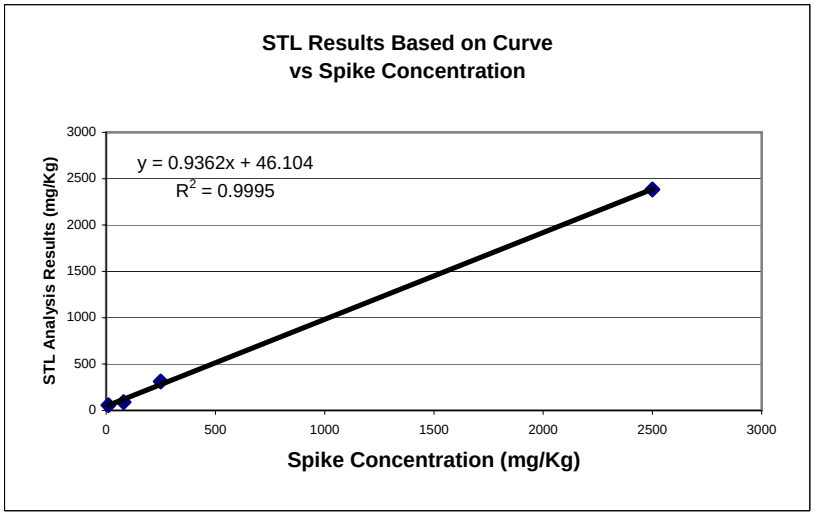
Figure 4-14

CRREL Calibration Plots for NC-Spiked Soil





CRREL Test Sample Plots for NC-Spiked Soil



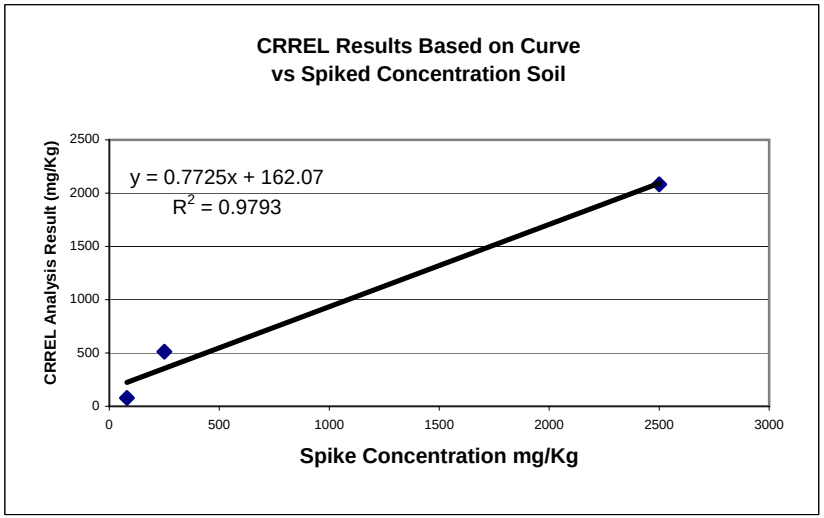
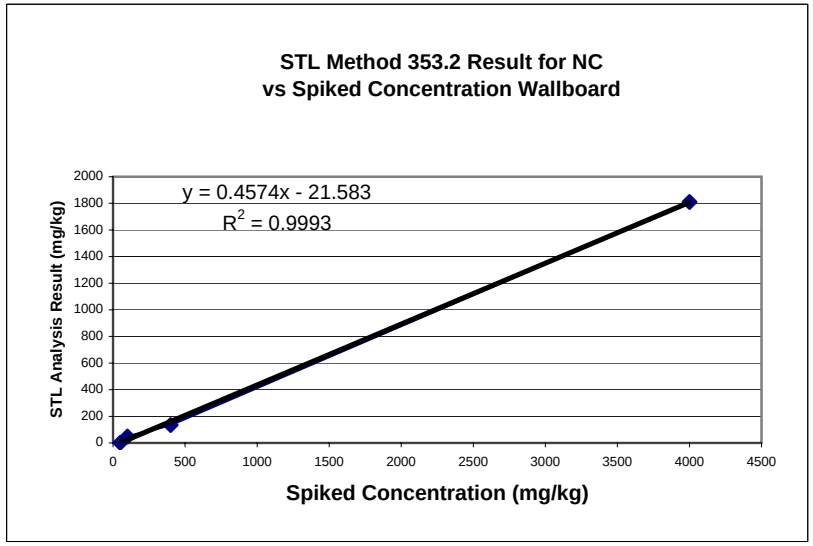
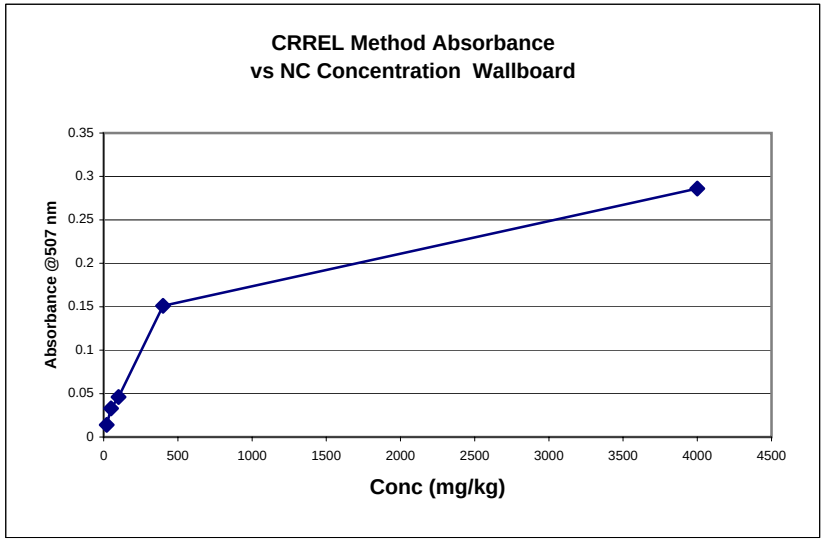


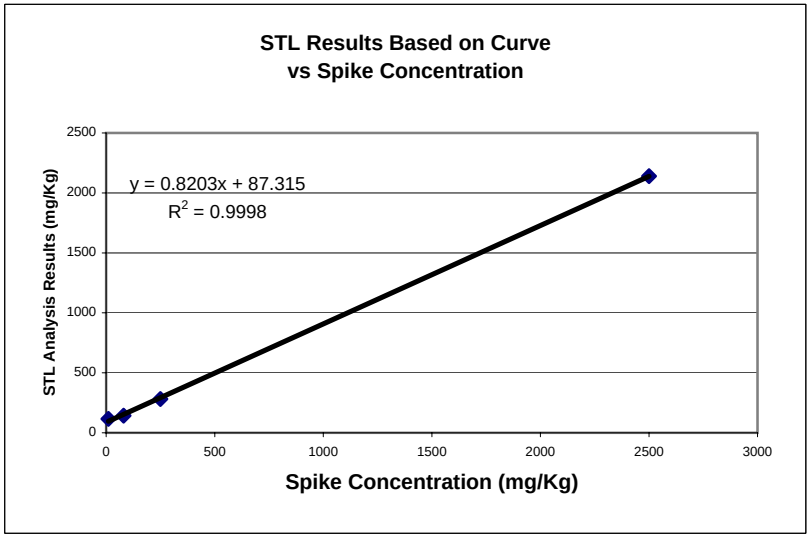
Figure 4-14

CRREL Calibration Plot for NC-Spiked Wallboard





CRREL Test Sample Plots for NC-Spiked Wallboard



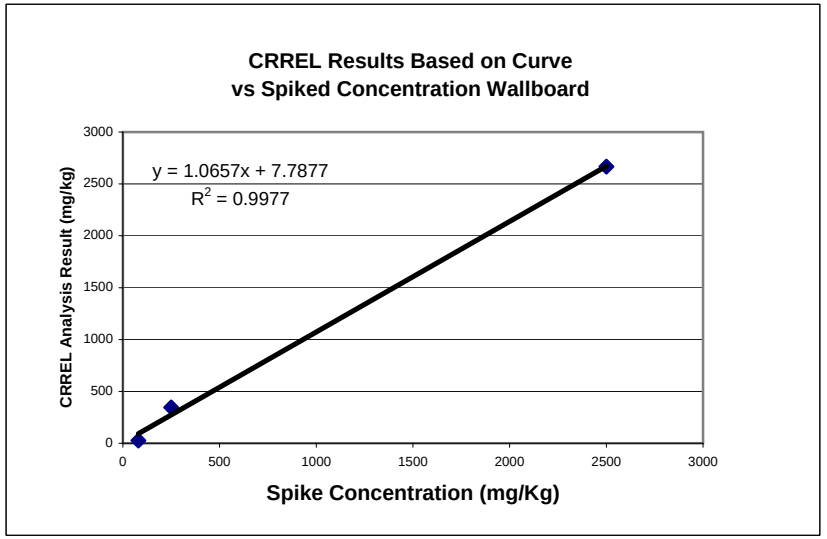
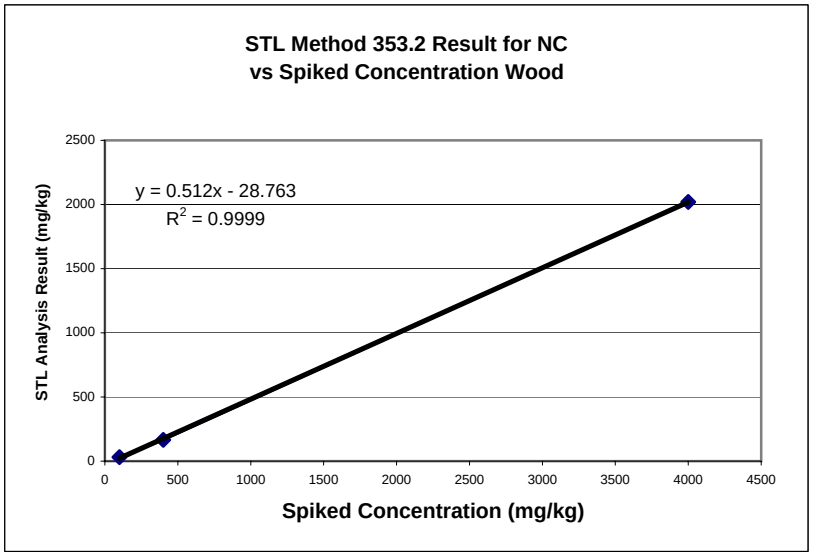
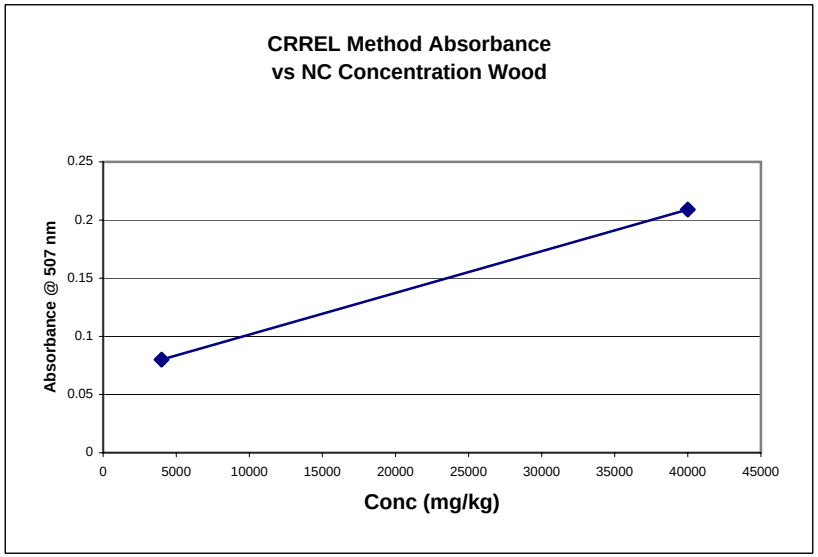


Figure 4-14

CRREL Calibration Plots for NC-Spiked Wood





CRREL Test Sample Plots for NC-Spiked Wood

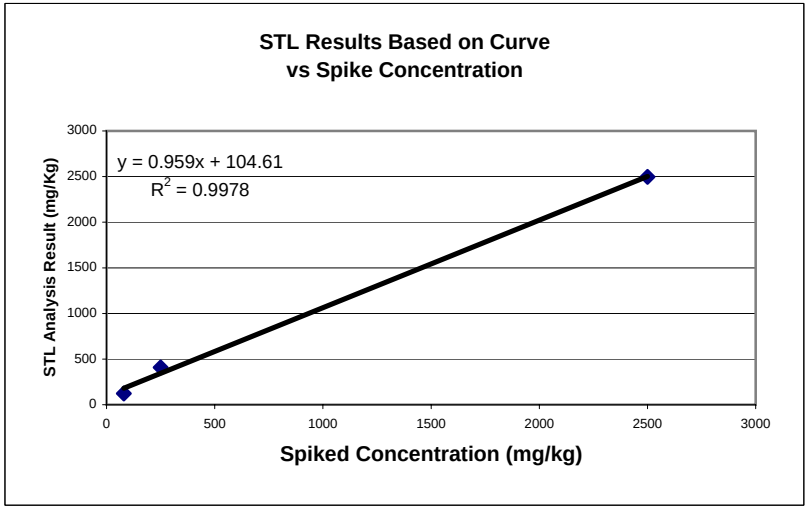
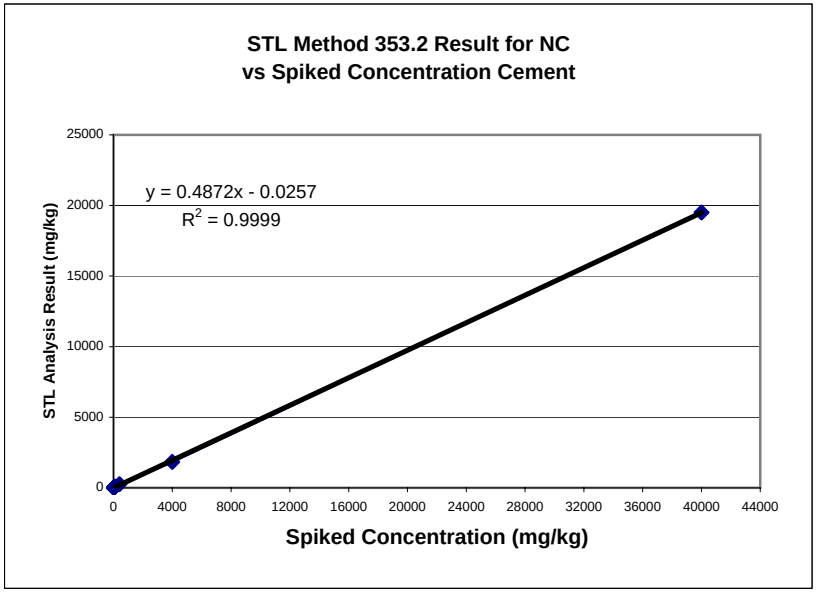
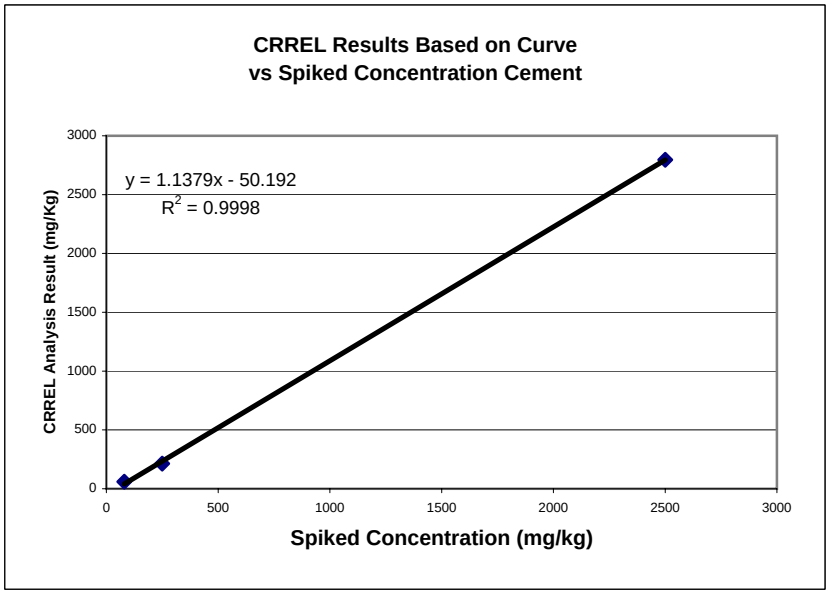


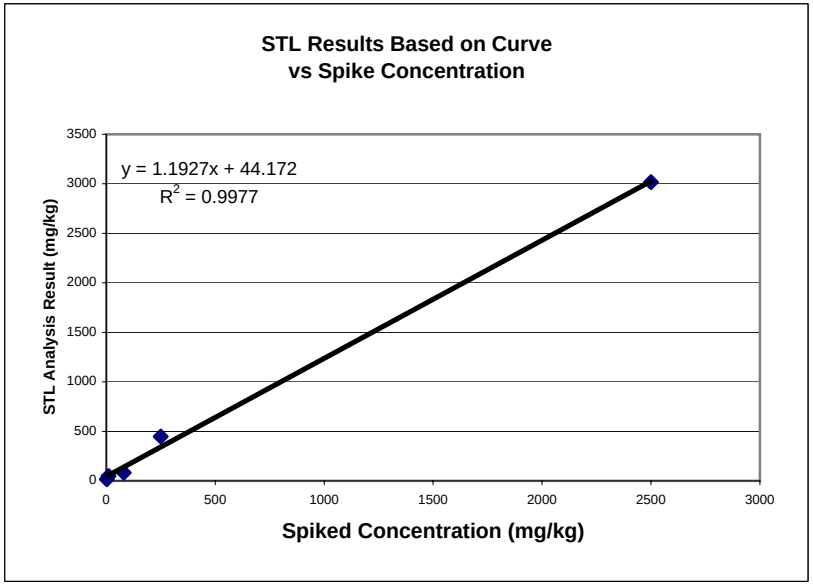
Figure 4-14

CRREL Calibration Plots for NC-Spiked Cement





CRREL Test Sample Plots for NC-Spiked Cement



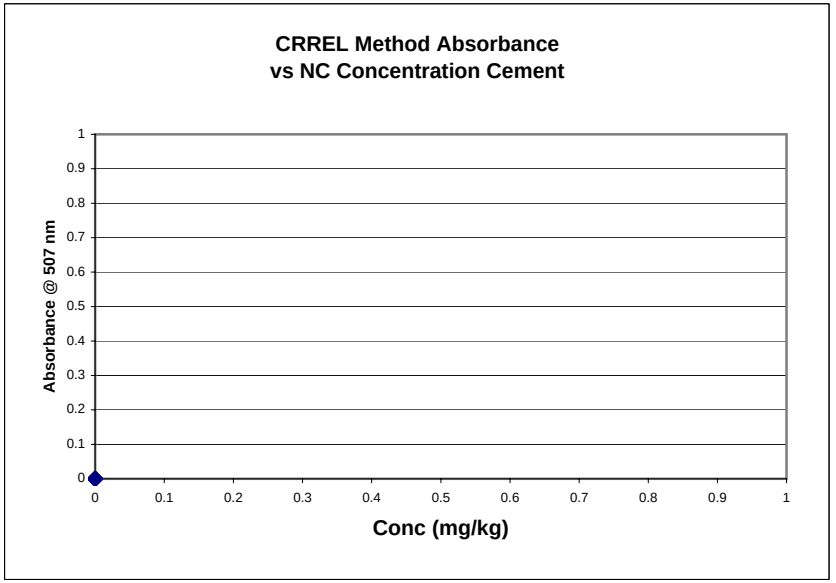
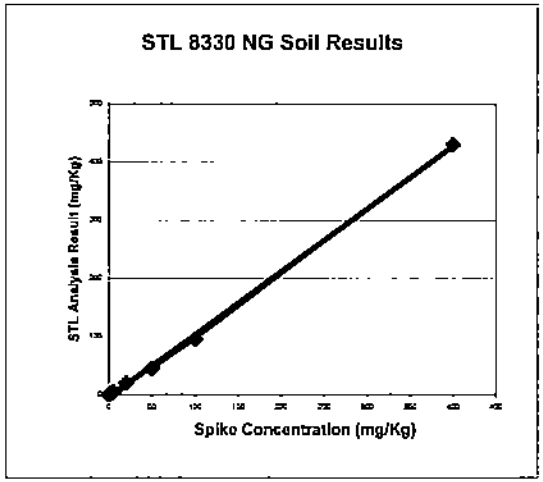
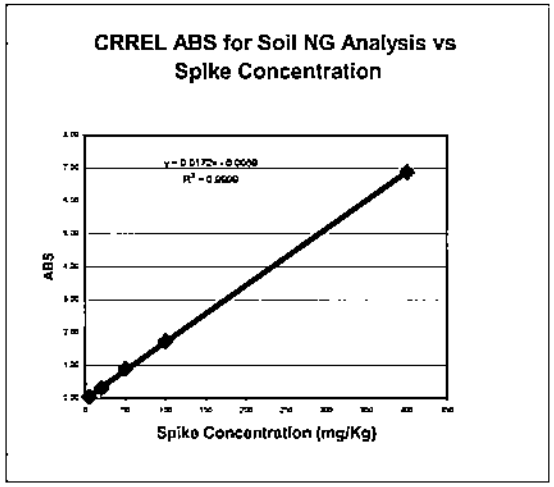


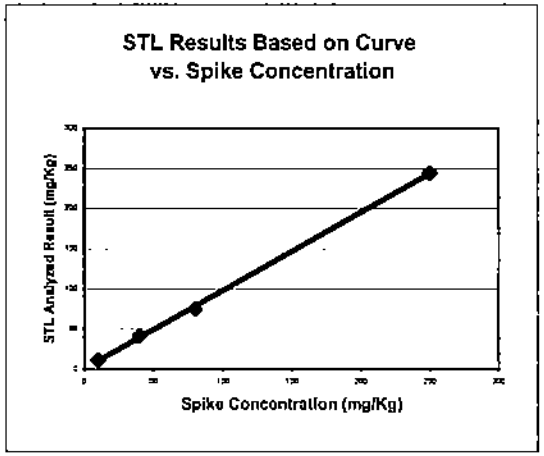
Figure 4-14

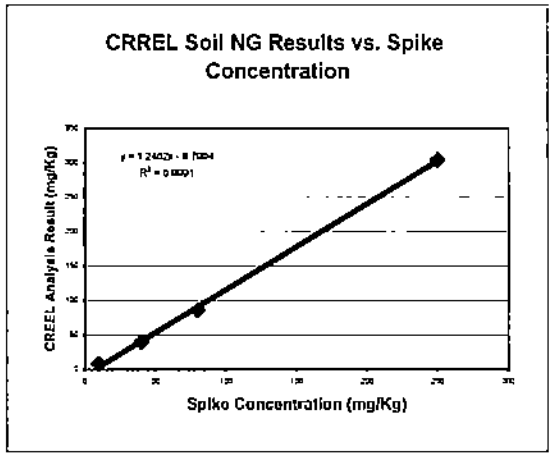
GC/TID Calibration Plots for NG-Spiked Soil





Test Sample Plots for NG-Spiked Soil





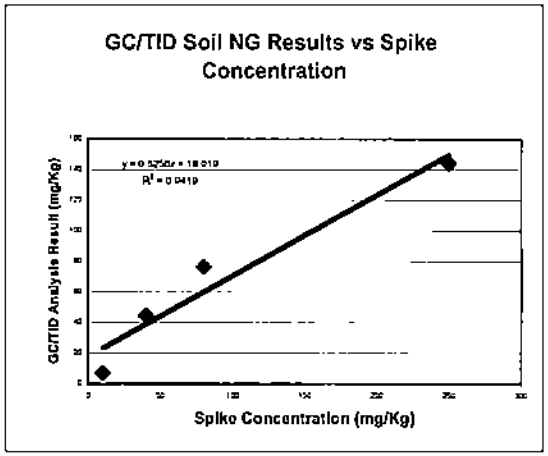
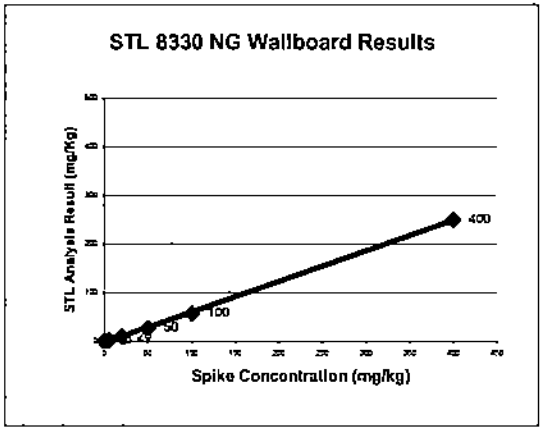
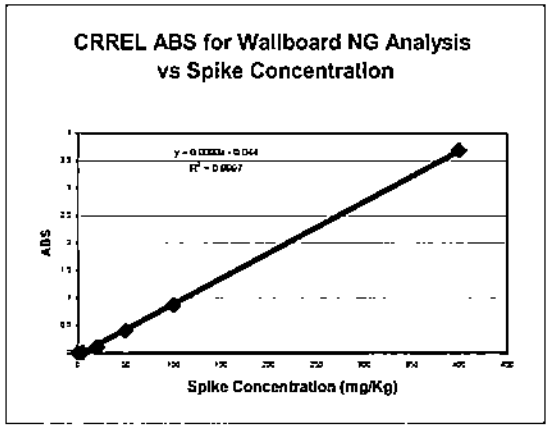


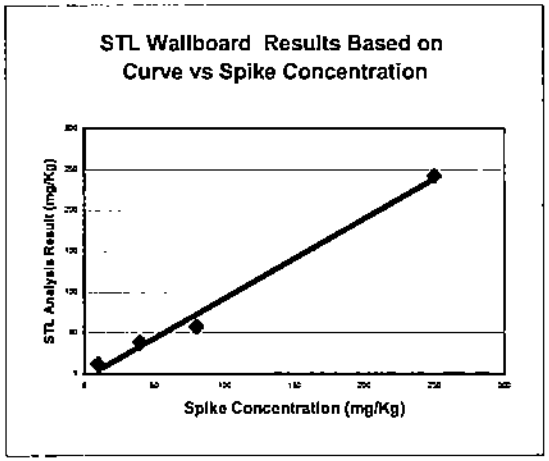
Figure 4-14

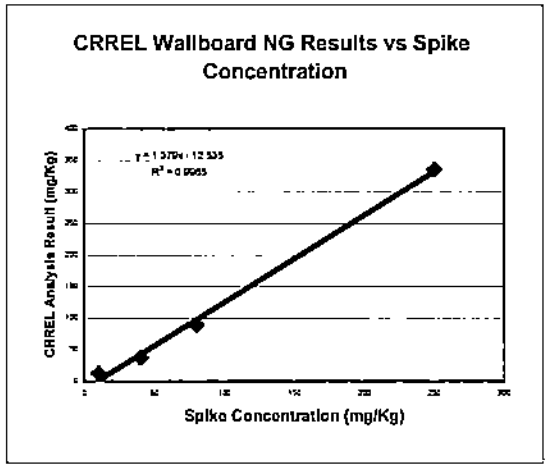
GC/TID Calibration Plots for NG-Spiked Wallboard





Test Sample Plots for NG-Spiked Wallboard





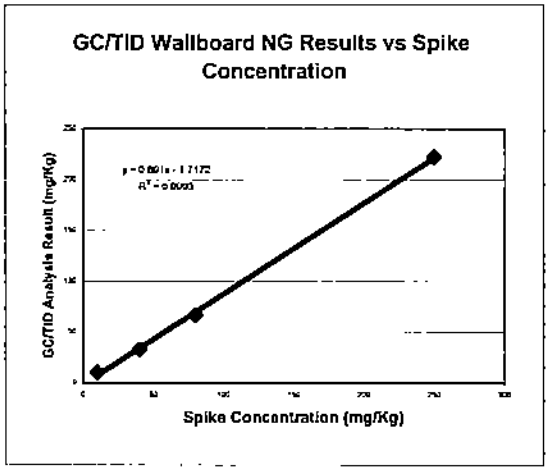
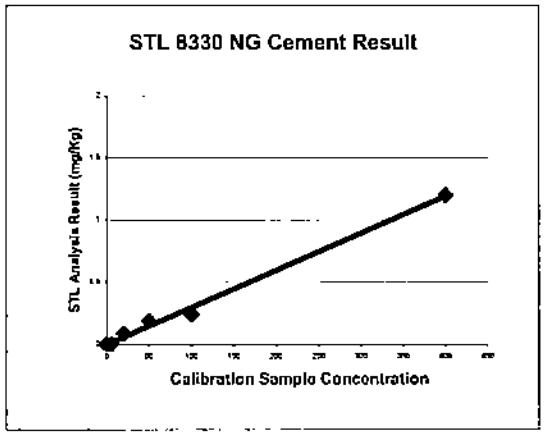
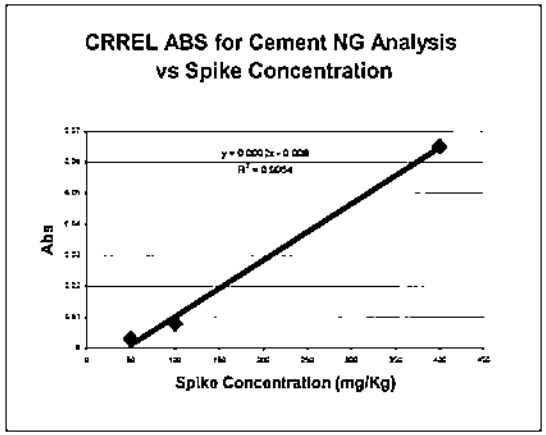


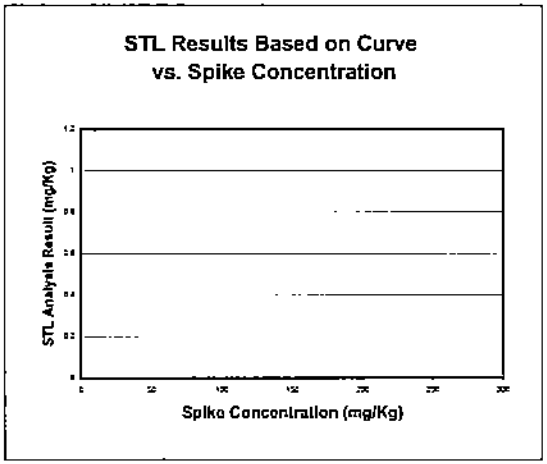
Figure 4-14

GC/TID Calibration Plots for NG-Spiked Cement





Test Sample Plots for NG-Spiked Cement



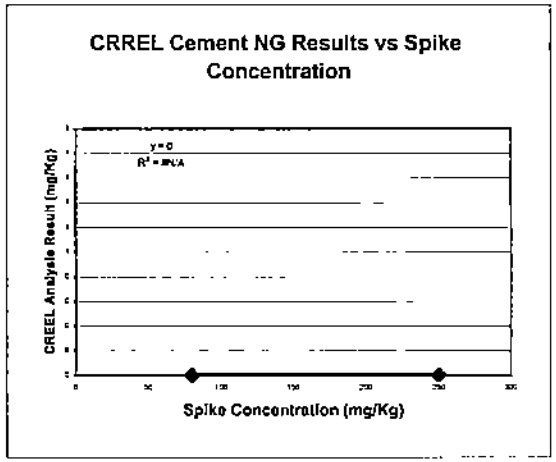
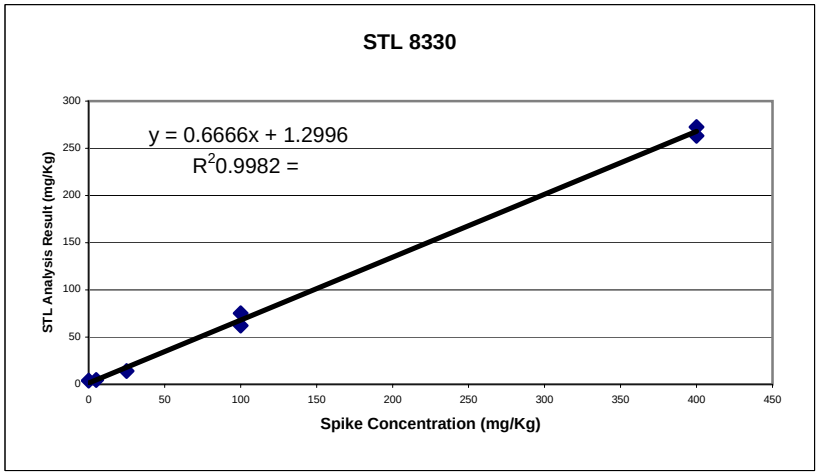
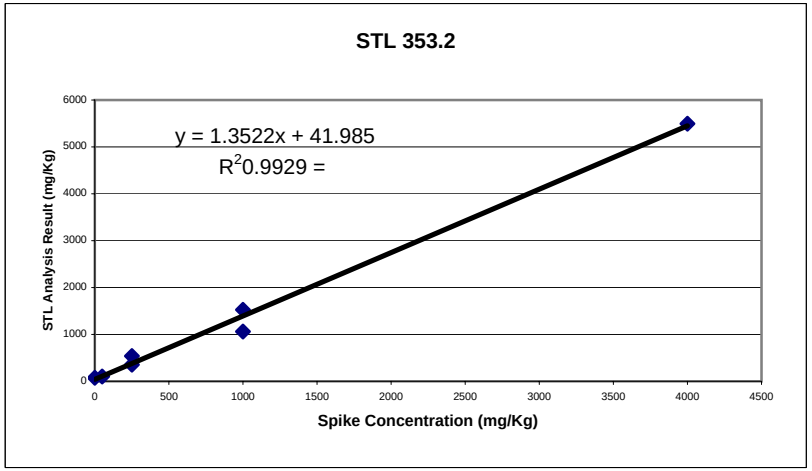


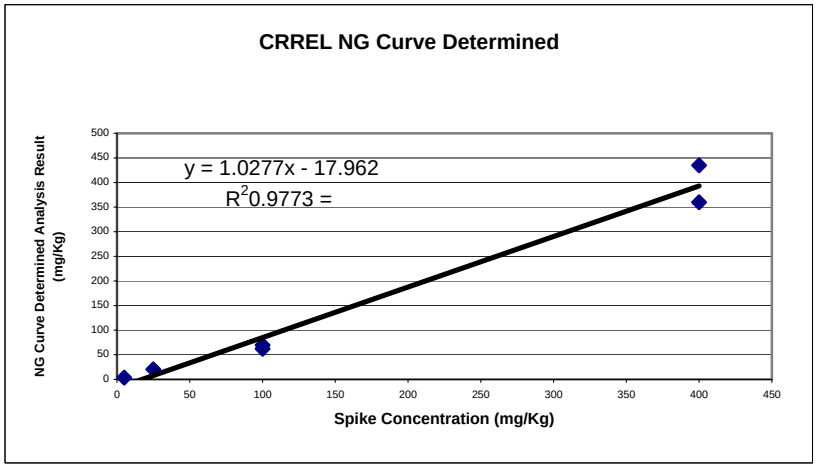
Figure 4-15

CRREL NC + NG-Spiked Test Sample Plots

Soil







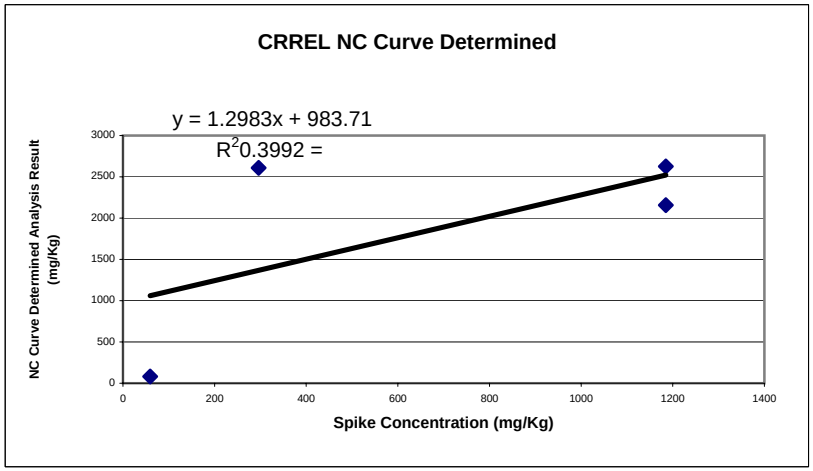
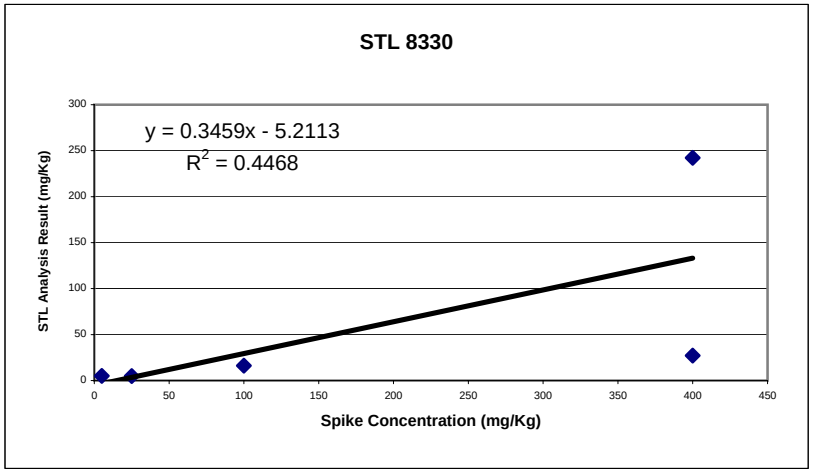
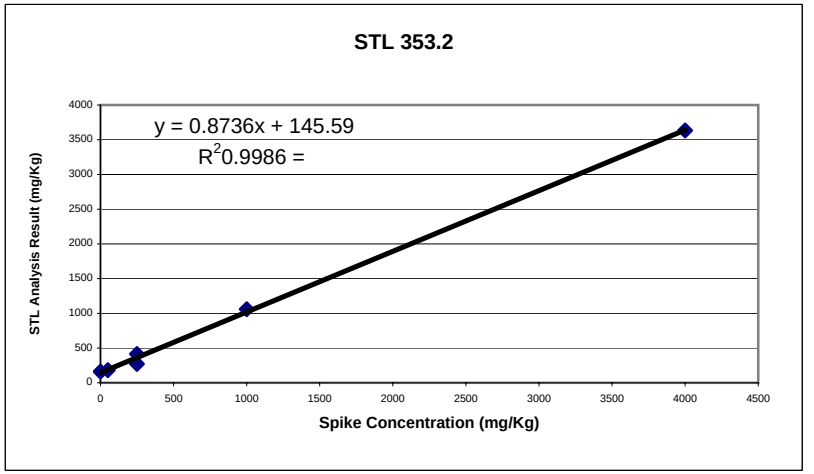
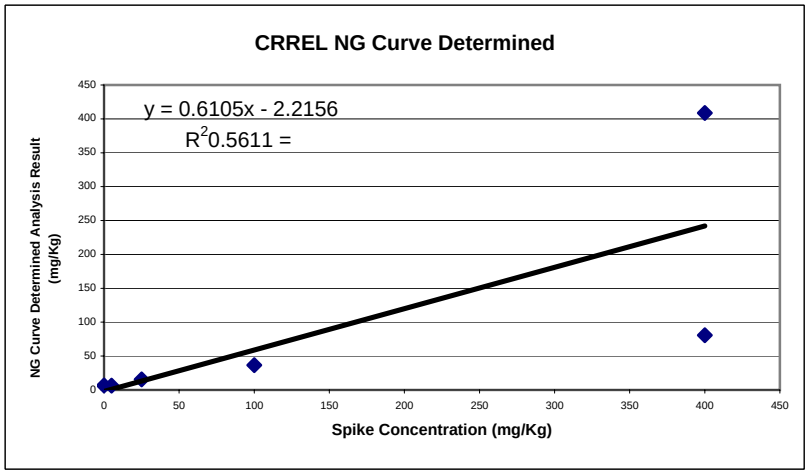


Figure 4-15

Wallboard







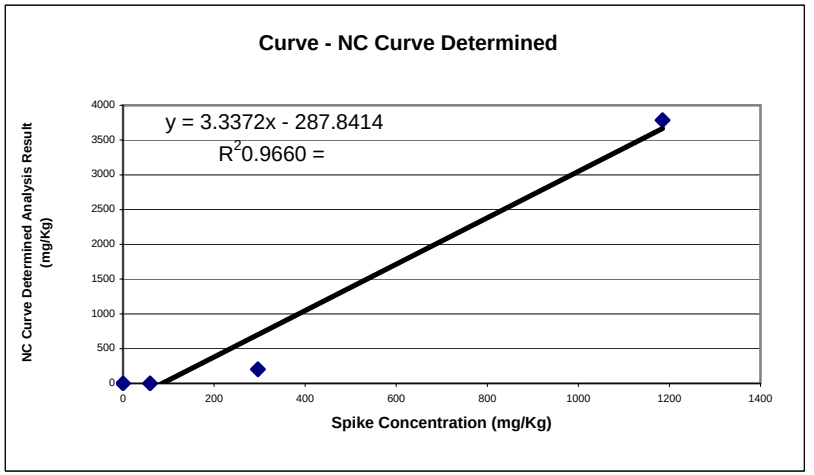
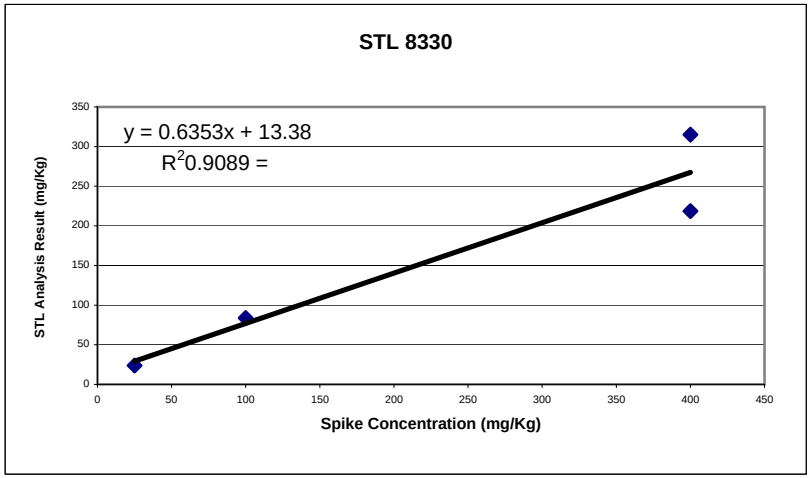
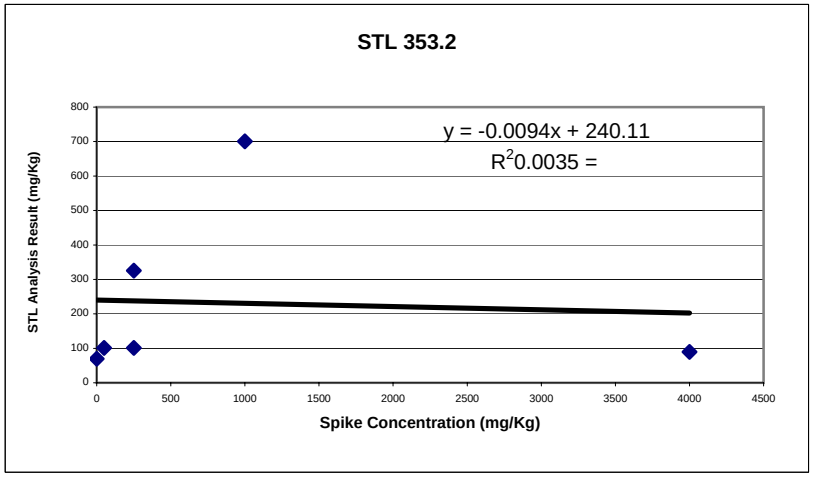


Figure 4-15

Wood





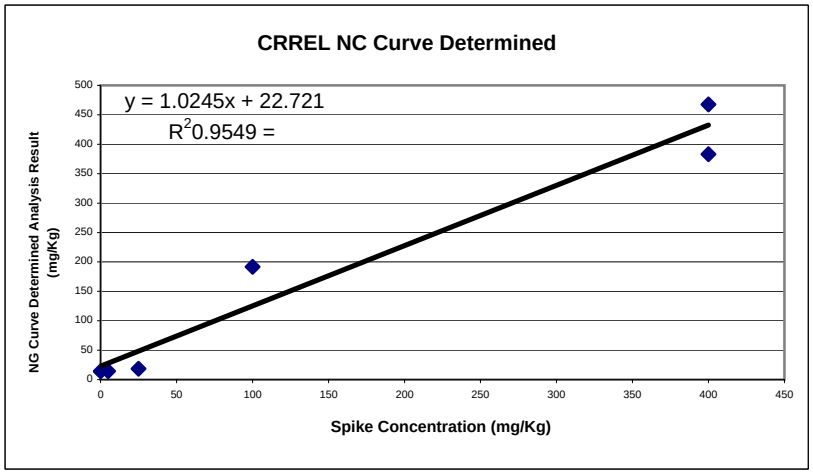
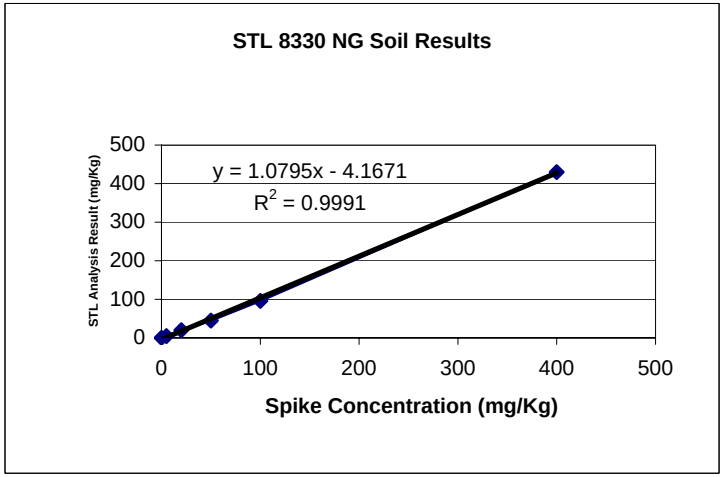
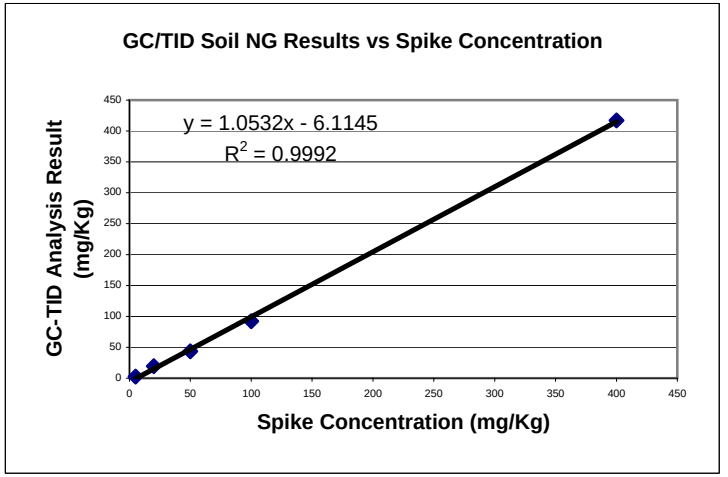


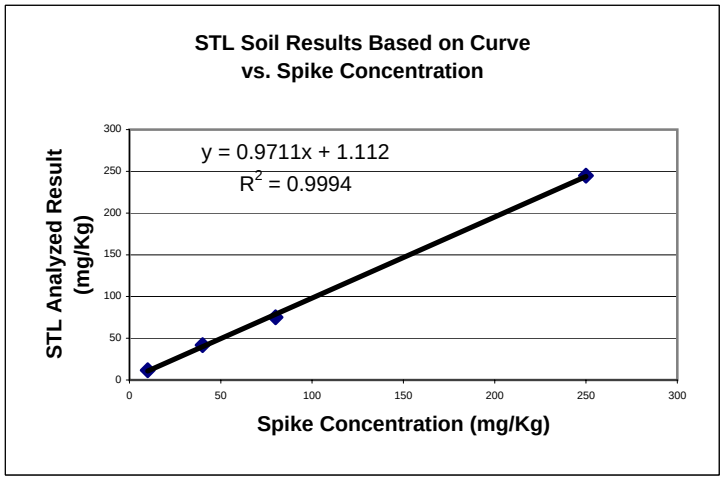
Figure 4-16

GC/TID Calibration Plots for NG-Spiked Soil





Test Sample Plots for NG-Spiked Soil



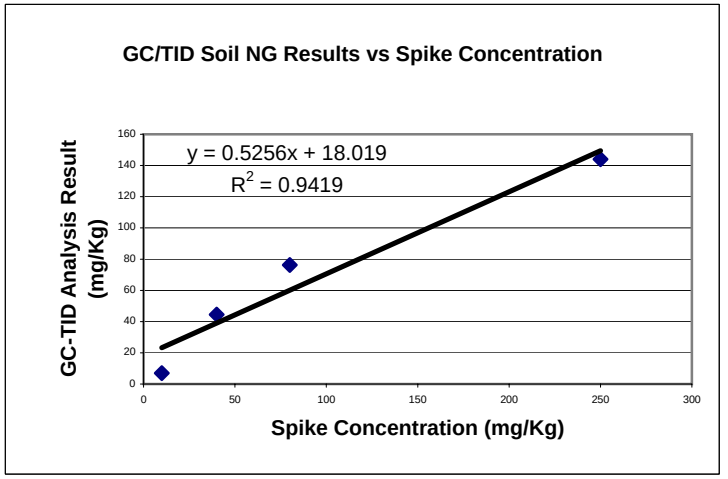
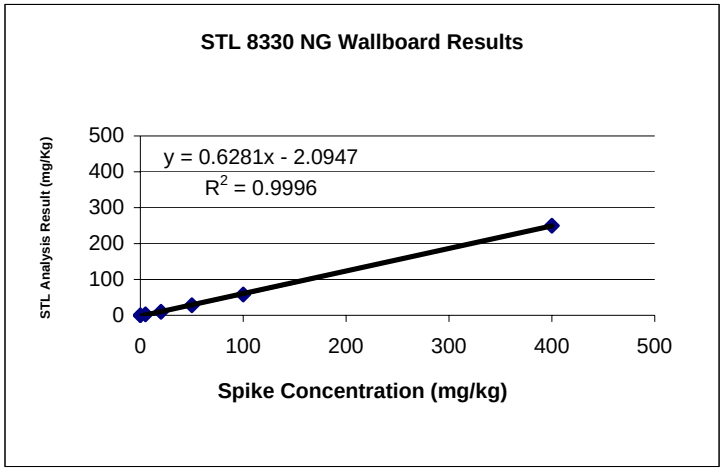
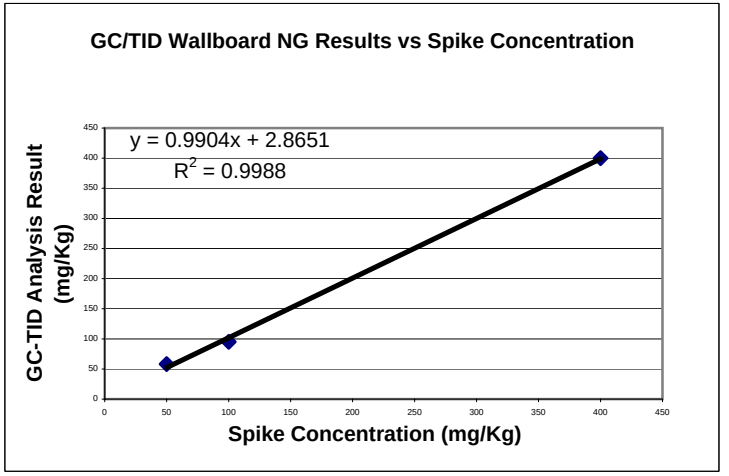


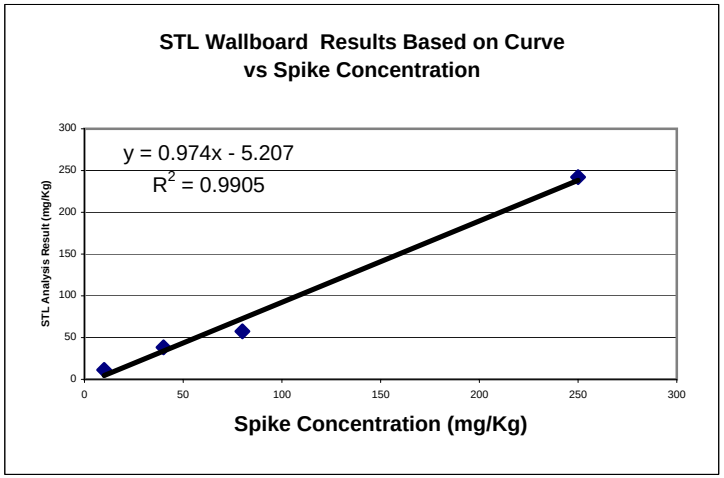
Figure 4-16

GC/TID Calibration Plots for NG-Spiked Wallboard





GC/TID Test Sample Plots for NG-Spiked Wallboard



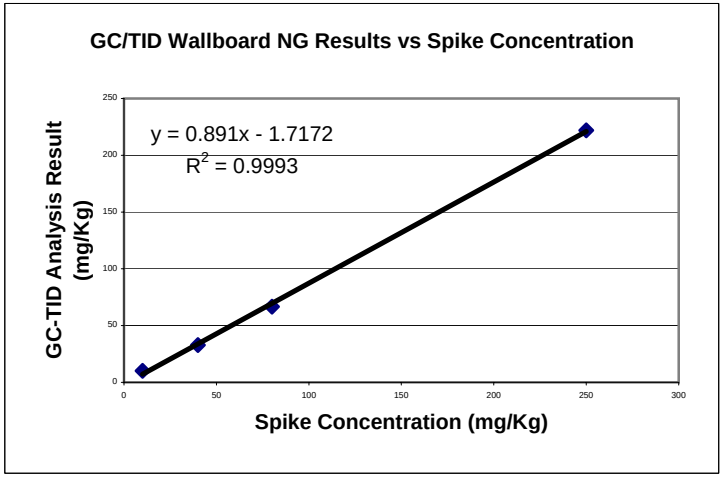
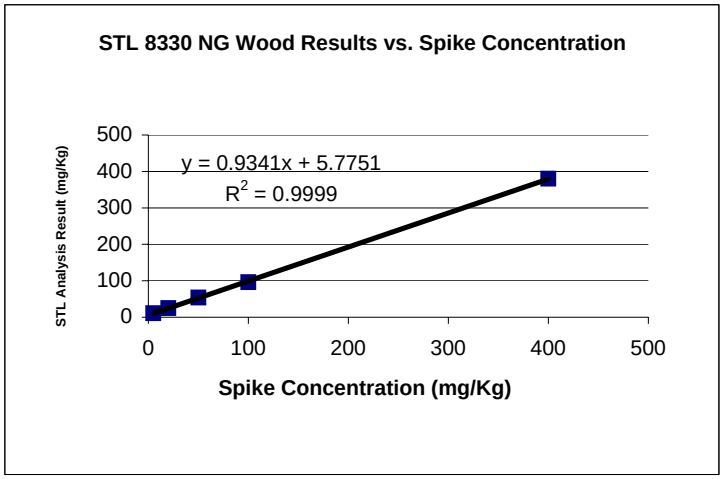
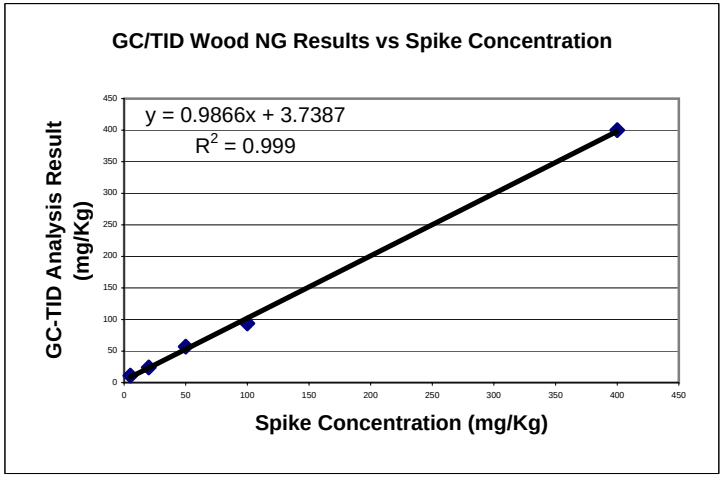


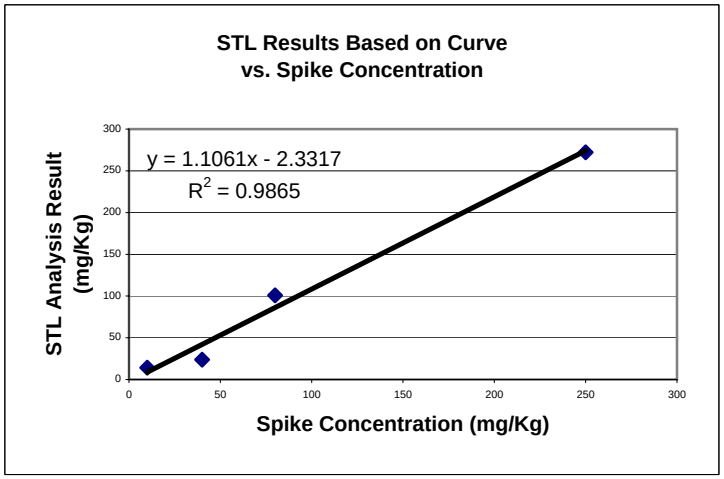
Figure 4-16

GC/TID Calibration Plots for NG-Spiked Wood





GC/TID Test Sample Plots for NG-Spiked Wood



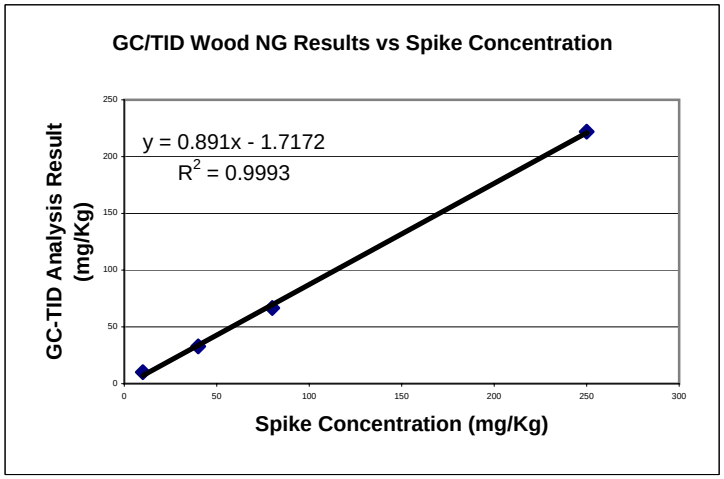


Figure 4-16

GC/TID Calibration Plots for NG-Spiked Cement

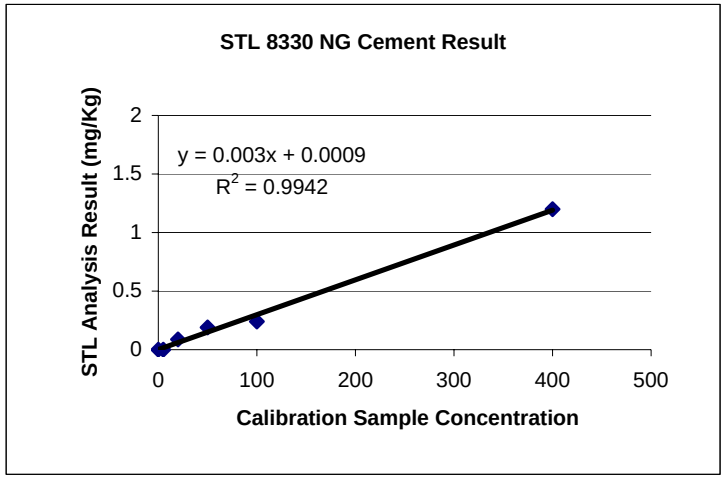
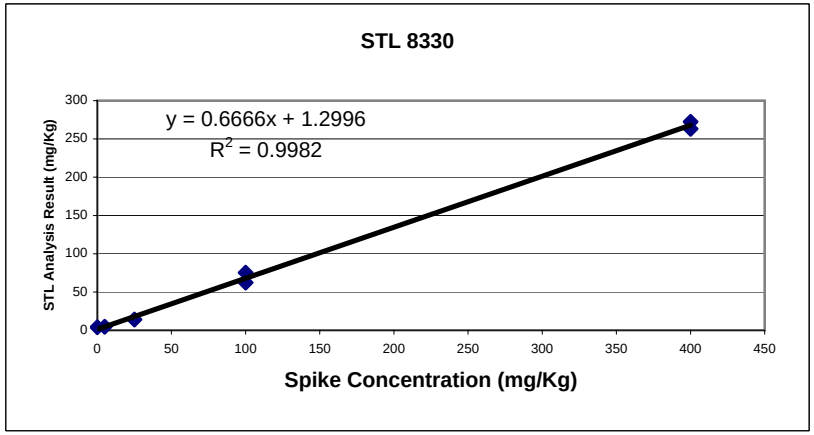
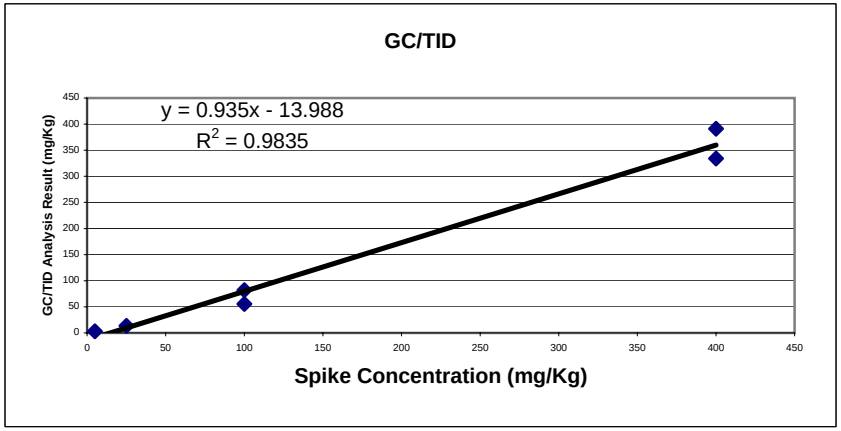


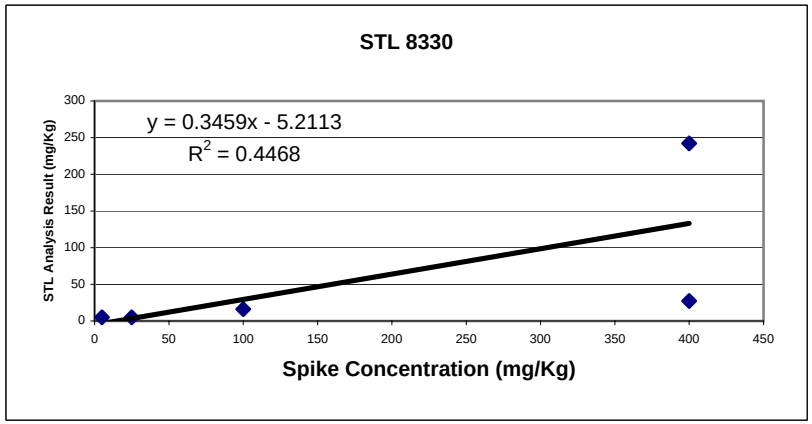
Figure 4-17

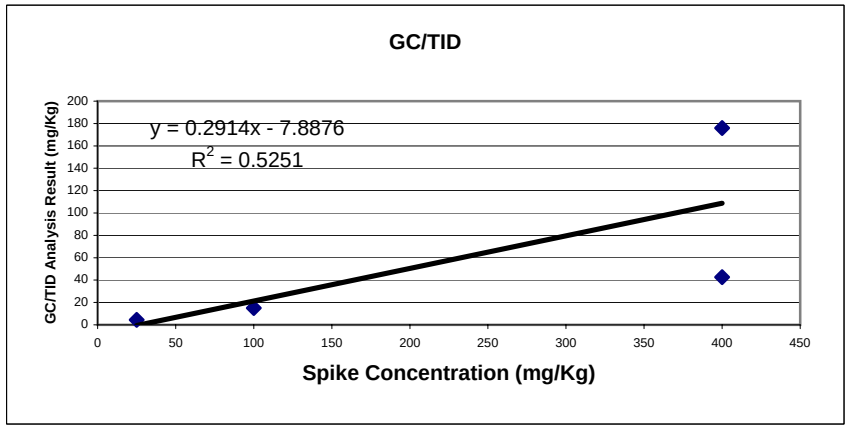
Test Sample Plots - NG + NC - Spiked - Soil



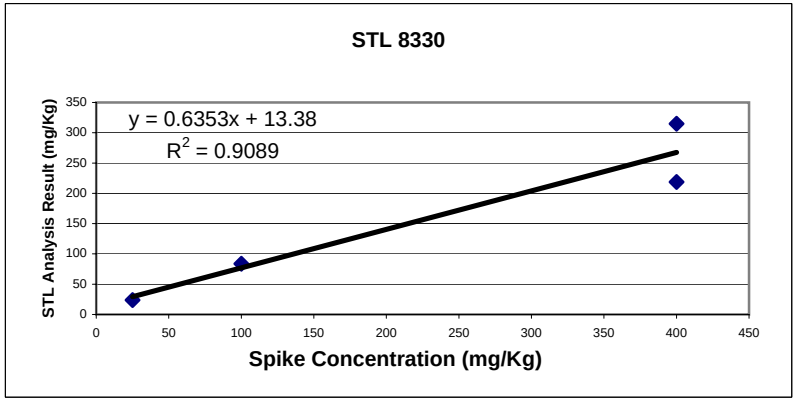


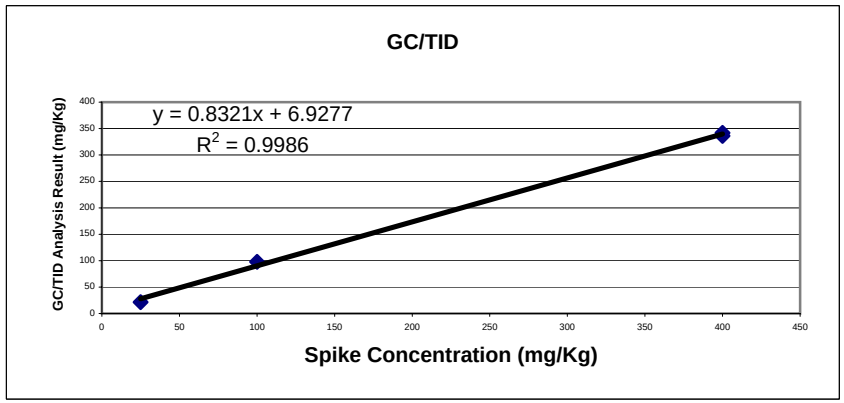
Test Sample Plots - NG + NC - Spiked - Wallboard





Test Sample Plots - Combined NG + NC - Spike - Wood





APPENDIX D

FIELD DEMONSTRATION REPORT

Environmental Security Technology Certification Program

Field Demonstration Report
Applied Innovative Technologies for Characterization of Nitrocellulose- and Nitroglycerine Contaminated Buildings and Soils

Badger Army Ammunition Plant
Baraboo, Wisconsin

January 5, 2007

Revision 1

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LIST OF ACRONYMS

BAAAP	Badger Army Ammunition Plant
°C	degrees Celsius
cm	centimeter
CRREL	Cold Regions Research and Engineering Laboratory
EPA	U.S. Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
EJM	Expansion Joint Material
F	Fahrenheit
g	gram
GC	gas chromatograph(y)
GC/TID	gas chromatograph(y) with thermionic ionization detection
HPLC	high-performance liquid chromatography
LCS	laboratory control sample
MCAWW	Methods for the Chemical Analysis of Wastewater
MS	matrix spike sample
MSD	matrix spike duplicate sample
mg/kg	milligrams per kilogram
mg/L	milligrams per liter
µL	microliter
mL	milliliter
mm	millimeter
NC	nitrocellulose
NG	nitroglycerine
nm	nanometer
psi	pounds per square inch
RDX	Royal Demolition Explosive, cyclotrimethylenetrinitramine
SRI	SRI Instruments, Inc.
SS	stainless steel
STL	Severn Trent Laboratories, Inc.
TDL	Technology Development Laboratory
TID	thermionic ionization detector
UXO	unexploded ordinance
SUXOSO	Shaw UXO Safety Officer

Acknowledgements

We gratefully acknowledge the hosting of this demonstration at the Badger Army Ammunition Plant. In particular we would like to thank the Installation Director Joan Kenney for her support. We would like to thank ESTCP for their guidance and support. We would also like to acknowledge the US Army Corps of Engineers personnel that assisted in the performance of the project, including Jay Hodges. Numerous Shaw employees contributed to this project including Dan Mckellin, Mike Clemens, Bill Eilbeck, Duane Root, Ellen Lay, Ed Morren and Steve Crouch.

Abstract

A field demonstration was conducted to assess the performance of three field analytical methodologies for the presence and/or concentration of nitrocellulose (NC) and nitroglycerine (NG) in soils as well as wood and concrete building materials collected at Badger Army Ammunition Plant (BAAAP) in Baraboo, WI. Acetone extracts of soils, concrete material, and wood samples were analyzed by each of the on-site methods and results compared to off-site laboratory analysis using high performance liquid chromatography (HPLC) with EPA SW-846 Method 8330 for NG and MCWAA Method 353.2 for NC, an automated colorimetric method. The field methods evaluated included EXPRAY™ and DROPEX^{Plus} colorimetric test kits (total NC/NG), CRREL RDX colorimetric test (proposed EPA SW-846 8510) (total NC/NG) and GC/TID field gas chromatograph (NG only). Accuracy of the qualitative methods was evaluated based on percent false positive / false negatives. The quantitative on-site methods were evaluated using linear regression analysis and relative percent difference (RPD) comparison criteria. The primary use of these analytical methods would be for characterization of explosive–contaminated buildings. Adequate characterization could allow many buildings to be left in place resulting in substantial cost avoidance and expedited transfer of properties out of Department of Defense (DOD) control. Findings from the field demonstration are presented.

FIELD DEMONSTRATION REPORT
APPLIED INNOVATED TECHNOLOGY FOR CHARACTERIZATION OF NITROCELLULOSE- AND NITROGLYCERINE CONTAMINATED BUILDINGS AND SOILS
BADGER ARMY AMMUNITION PLANT
BARABOO, WISCONSIN

SHAW ENVIRONMENTAL & INFRASTRUCTURE, INC.

January 5, 2007

1.0 INTRODUCTION

1.1 Background

Badger Army Ammunition Plant (BAAAP) is one of many inactive Army ammunition plants currently under the control of the Department of Defense (DOD) with transitioning missions in place. These plants are in varying stages of transfer out of DOD control. In order to transfer these properties, DOD must characterize and decontaminate the properties to a level protective of human health and the environment. To accomplish this task, many buildings used in the production, loading, handling, and storage of explosives will have to be demolished or characterized and decontaminated. BAAAP alone has more than 1,400 buildings on the installation that have to be addressed. The contaminants of concern associated with the buildings at BAAAP include nitrocellulose (NC), nitroglycerine (NG), dinitrotoluene (DNT), and common environmental compounds such as asbestos-containing material (ACM), solvents, and metals.

1.2 Study Objectives

The objectives for the Environmental Security Technology Certification Program (ESTCP) demonstration are to evaluate and document the performance of three distinct candidate experimental fields analytical methods for detecting and quantifying NC and NG associated with structural concrete pads, underlying soils, and structural building materials such as framing timbers and wallboard. With adequate characterization, many buildings could be safely left in place or building materials salvaged resulting in substantial cost reduction and the ability to transfer the properties out of DoD control more quickly**.** A secondary purpose for some of the demonstration concrete and soil samples was to provide NG and NC data for specific locations awaiting demolition safety clearance. The technologies evaluated in the field demonstration included: DROPEX^{Plus}/EXPRAY™ colorimetric indicator, gas chromatography with thermionic ionization detection (GC-TID), and the Cold Regions Research and Engineering Laboratory (CRREL) Royal Demolition Explosive (RDX) colorimetric field screening method.

1.3 Regulatory Issues

There are no regulatory drivers per se governing this project. Nor are there state or federal environmental standards for NC and NG cleanup. There is a site-specific Wisconsin Department of Natural Resources (WDNR) cleanup criterion for NG in the area soils of 3.6 milligrams per kilogram (mg/kg) (EPA & WDNR, 1988). There is no DoD standard for NC and NG residual contamination; however, safety concerns related to the explosive nature of these materials provide the driver for this investigation.

The Department of Army Industrial Operations Command Pamphlet IOCP-385-1 (1997) defined building explosives contamination as follows:

- 1X – (X) level of contamination. This level applies to articles, equipment or buildings subjected to only routine, after-use cleaning. Substantial contamination (explosive residue) continues to exist.

- 3X - (XXX) level of contamination. This level applies where cleaning has removed surface contamination, but significant amounts (enough to present an explosive safety hazard) may remain in less obvious places. The article, equipment or building is safe for its intended purpose.

- 5X - (XXXXX) level of contamination. This level applies when no significant amounts (enough to present an explosive safety hazard) of contaminants remain. The article, equipment or building does not pose an explosive hazard and is safe for welding, drilling, sawing, etc., and sale to the general public.

- 0 – (zero) level of contamination. This level applies when the articles, equipment or buildings were never contaminated,

Figure 1-1 BAAAP Building with XXX (3X) Classification

The 1X level of contamination is not clearly defined, but it is interpreted to mean that the potential for substantial contamination exists and there is also the potential of an explosive safety hazard. At BAAAP alone, over 900 of the buildings have been classified as 3X. Pamphlet IOCP-385-1 further states that up through the early 1990s, each time production ceased at government-owned explosive production facilities, managers assumed that they would need facilities and equipment in the future and preserved them. The contamination status decisions on

buildings and equipment were simple. Classifiers marked almost everything as 3X (see Figure 1-1), even if uncontaminated. This was the simplest, most economical course when keeping everything for its original purpose. In the 1990s, the assumption changed (that the Army will always keep the production facilities), and Army began the process of transferring property and equipment. In 2004, Plexus Scientific surveyed over 800 buildings and either confirmed or reclassified these structures to 1X, 3X, or 5X.

The 1X, 3X, 5X and 0 system of building classification is still visible on markings at the site, but it is no longer used and the classification has been replaced with "Safe and "Hazardous" terminology as defined by Army documentation: TB 700-4 and DODI 4140.62.

1.4 Stakeholder/End-User Issues

By verifying these technologies, stakeholders will have additional tools that will aid in the decision-making process for transfer of property at BAAAP. The demonstration, if successful, will help streamline the property disposal process.

1.5 Previous Testing

A previous ESTCP demonstration was performed between April 28, 2002 and May 13, 2002. The 2002 demonstration of candidate field test methods included Raman spectroscopy, EXPRAY™ colorimetric indicator, and the CRREL RDX colorimetric field screening method were used to test for the presence and/or concentration of NC or NG in soil samples and concrete slabs. Attempts were made to compare the results from these field measurements to laboratory analyses of NC and NG in the same materials to evaluate the reliability of the field screening and analytical methods for identifying and quantifying NC and NG in buildings and soils. Raman spectroscopy was also used for identifying the presence of other organic compounds used in the manufacturing processes conducted in the study area.

The results of the previous demonstration and lessons learned were presented in the *Phase I Final Report, Rocket Paste Production Building Investigation, Badger Army Ammunition Plant, dated June 24, 2003, and published by Stone & Webster, Inc.* (Stone & Webster, 2003). Due to a number of factors, including the lack of energetic compounds in the buildings used for the demonstration, attempts at validation of the field methods for detection of these materials were inconclusive.

This Demonstration will apply lessons learned during the BAAAP 2002 demonstration to obtain results that would allow validation of the field analytical techniques. One of the major findings during the previous demonstration was that the building(s) selected for the demonstration must have sufficient residual energetic material in place to adequately apply the test methods. The buildings selected for this demonstration were used directly in the production or use of energetic materials and present a variety of potential contamination sites and locations that may likely serve as specific accumulators of contamination residue.

Prior to the field demonstration, a bench scale study of the experimental technologies was conducted by Shaw Environmental & Infrastructure, Inc. (Shaw) and results were described in a bench test report (Shaw, 2005). The technologies evaluated at the bench scale level included Raman spectroscopy, DROPEX^{Plus}/EXPRAY™ colorimetric indicator, GC-TID, and the CRREL RDX colorimetric field screening method. Uncontaminated soil and building materials (concrete, wood, and wallboard) from the BAAAP site were spiked with known amounts of NG,

NC and NC/NG combined at specified levels. Splits of these samples were submitted to Severn Trent Laboratories, Inc. (STL) in Sacramento, CA for analysis by reference methods for comparison. The results of the Bench Scale tests were presented in the *Draft BAAAP Bench-Scale Treatability Report for Applied Innovative Technologies for Characterization of Nitrocellulose and Nitroglycerine Contaminated Buildings and Soils, dated November 2005* (Shaw Bench Test, 2005). Results from the bench scale tests were used to optimize the testing and analysis processes for the subsequent field demonstration.

2.0 DEMONSTRATION APPROACH

2.1 Demonstration Site / Facility Description

Shaw Environmental & Infrastructure, Inc. (Shaw) as the prime contractor to the U.S. Army Corps of Engineers Omaha District (USACE) performed the field demonstration testing for the U.S. Department of Defense Environmental Security Technology Certification Program (ESTCP). The demonstration took place at BAAAP, located on 7,354 acres of land in Sauk County, Wisconsin. Laboratory personnel from the Shaw Technology Development Laboratory (TDL) located in Knoxville, Tennessee conducted the field analysis on soil, concrete and wood samples collected from and around production buildings as selected on site from December 1, 2005 to December 19, 2005. A description of the on-site analytical methods employed and a comparison of results and method performance considerations are presented in this report to compare qualitative and quantitative field analysis results with the laboratory reference methods results obtained for NG and NC and to determine if they can be used wholly or partially in lieu of conventional demolition, removal and clearance using the laboratory reference methods. All testing was conducted in general accordance with the ESTCP Demonstration Plan, April 28, 2005 Revision 2, Applied Innovative Technologies for Characterization of Nitrocellulose and Nitroglycerine Contaminated Buildings and Soils, Badger Army Ammunition Plant, Baraboo, Wisconsin (Shaw Work Plan, 2005). Exceptions to the work plan were as follows: no Asbestos Containing Material (ACM) was tested due to safety issues related to crushing of ACM and Raman spectroscopy was not used due to safety issues related to heat generation noted during the bench scale testing.

Figure 2-1 BAAAP Shaw Lab Trailer Location on Site

A Shaw 28 foot mini- mobile lab trailer was delivered to the BAAAP site on November 29, 2005 for the 2 week ESTCP demonstration. The trailer was located on site at the end of a short dead-

end road extending north from the main gate road off of Hwy 12 and was one mile east of Hwy 12. It was just east of a row of five production buildings and was bound by field to the north and further east. The trailer was powered by a Wagner diesel powered 100 (kilovolt-amp) KVA generator with a 240 Volt single phase output supplied by a local equipment rental company. The trailer came equipped with a fume hood and small refrigerator. The trailer set-up is shown in Figures 2-1, 2-2, and 2-3

Figure 2-2 Shaw Lab Trailer and Generator On-site

Figure 2-3 Testing Inside Lab Trailer

Additional instrumentation and testing equipment shipped to the site by Shaw Lab personnel included a drying oven, a bench top shaker table, an analytical balance, a SRI Instruments, Inc. (SRI) portable field GC/TID, and a HACH DR 2010 portable spectrophotometer. Miscellaneous lab and sampling supplies were either purchased locally or ordered and delivered from a laboratory supply company.

An onsite concrete bunker located 100 yards from the mobile lab was used for sample storage and breaking concrete cores. Samples were secured inside the bunker during the demonstration and prior to testing. Temperatures inside the bunker ranged from minus 10 to 20° F. Outside and inside the bunker is shown in the pictures below, Figures 2-4 and 2-5.

Figure 2-4 BAAAP Storage Bunker

Figure 2-5 Wood Samples Inside Bunker

2.2 Demonstration Objectives

The purpose of the demonstration is to evaluate the reliability of field technologies for NC and NG detection in building materials and soil. The technology verification will result in building characterization procedures that may benefit many U.S. Army ammunition plants with similar explosive materials. The implementation of these procedures may also result in substantial savings over conventional remedial investigation techniques of explosive-contaminated buildings. The objectives of the study are as follows:

- Compound Identification: Compare the accuracy, feasibility, strengths, and weaknesses of on-site field instrumental and analytical techniques for identifying and measuring NC and NG in or on building materials, foundations and soils.

- Compound Quantitation: Evaluate field data obtained for NC and NG using the quantitative CRREL RDX method and the reference laboratory Methods for the Chemical Analysis of Wastewater (MCAWW) 353.2 for NC and (EPA) SW-846 Method 8330 method for NG using samples of soil, concrete and wood collected at the BAAAP site.

- Compound Quantitation: Evaluate the repeatability of the quantitative analytical results between the ESTCP demonstration methods for NG detection (CRREL RDX method, EPA SW-846 Method 8330, and GC/TID).

- Evaluate the repeatability of qualitative NC detection results of the DROPEX^{Plus} and EXPRAY™ screening methods and quantitative testing using MCAWW 353.2 for NC (i.e., determine the likelihood of false positive or false negative results from the screening methods versus the laboratory quantitative analytical results).

- Evaluate the repeatability of qualitative NG detection results between the DROPEX^{Plus} and EXPRAY™ screening methods and quantitative testing using U.S. Environmental Protection Agency (EPA) SW-846 Method 8330 and gas chromatography (GC)/thermionic ionization detector (TID) for NG (i.e., determine the likelihood of false positive or false negative results from the screening methods versus the quantitative analytical results).

- Evaluate the repeatability of quantitative analytical results between the ESTCP demonstration methods for NC detection (CRREL RDX method and the MCAWW 353.2 method).

2.3 Testing Design and Description

A field demonstration of analytical procedures for NG and NC in soil and building materials was performed to verify the usability of the work flow in a technology demonstration for field characterization of buildings used in the production of NC and NG.

2.4 Sampling Plan

At the time of converting the BAAAP facility to standby status, buildings at BAAAP were classified by their assessed level of contamination. A recent survey of the buildings was conducted by the Army to verify these classifications. Some buildings have never been used for explosive material production and others were assigned designations based on the possible level of exposure to these materials. Many of the plant buildings were constructed of the same materials (Figures 2-6a and 2-6b).

2.4.1 Sample Locations

The primary objective of sampling at BAAAP was to obtain samples typically encountered in munitions remediation projects which would provide measurable levels of NG and NC for comparison of field analytical methods to established methodologies. However it was not a requirement that all samples contain both NC and NG. Three matrices of interest for the BAAAP ESTCP project were concrete, wood and soil. A secondary purpose for some of the concrete and soil samples was to provide some NG and NC data for specific locations awaiting demolition safety clearance.

Sample locations were chosen based upon input from the Shaw UXO Safety Officer (SUXOSO), field wipe tests using the DROPEX^{Plus} field analytical method, and areas of interest requested by Army personnel.

Figure 2-6a and Figure 2-6b Typical Structures Found at BAAAP

The SUXOSO, who had previously performed characterizations of buildings on BAAAP for energetic materials, supervised all activities during sampling. Some buildings listed in the initial

sampling list were not sampled because there was no indication of measurable contamination from field wipe tests performed by the SUXOSO.

The samples collected for the building investigation portion of the demonstration are summarized below in Table 2-1.

Demonstration Building Selection

The sampling process of the building investigation portion of this demonstration was designed to determine the presence or absence of NC or NG compounds within the concrete floors or foundations, in the soils under the concrete, or in the structural materials of the buildings that were selected for the study. Buildings were selected for the demonstration based on the likelihood that the compounds may have entered the concrete, soils or structural materials as a result of the physical processes conducted in them. Samples were selected based on the likelihood of NG, NC or NG and NC, but did not necessarily require the presence of both for the study. A total of 103 samples were collected: thirty three samples of wood, thirty three samples of soil, and thirty-seven concrete samples were collected during the demonstration.

Samples for the building investigation demonstration were taken from the following areas as summarized below in Table 2-1:

Table 2-1 Sample Summary

Building Name (Process Line)	Building ID No.	Wood Samples	Concrete Samples	Soil Samples	Duplicate Samples (A)[1]
Neutralizer House (NG)	6657-02N	2			
Nitrate House (NG)	6657-02I	2			1
Boiling Tub House (NC)	5024	7			
Pre Dry House (NC, NG)	6709-17	10			1
Powder Storage Pit (NC, NG)	9590	3	1		1
Box Wash House (NC, NG)	1890-01	9	9	3	3
Box Storage Houses (NC, NG)	1885-01, -02, 03		3, 14, 10	0, 25, 5	4
Total Samples Collected		**33**	**37**	**33**	**10**

[1] Duplicate samples were prepared from splits of the parent sample after collection and identified with an (A) added to the sample identification number.

Refer to Table 2-2 Sampling Log Summary Table below for sample details. See also Appendix B.1 for copies of sampling location maps of the selected building.

Table 2-2 Sampling Log Summary Table

Field Sample Identification #	Map ID Number	Sample Matrix	Sample Description	Comments
6657-02N-WD-001	1	Wood	upper room - wooden railing near floor	
6657-02N-WD-002	2	Wood	lower room - wooden railing near floor	
6657-02I-WD-003	3	Wood	liquid transfer trough wooden support	
6657-02I-WD-004	4	Wood	transfer trough cover - bottom (inner) side	
5024-000-WD-005	5	Wood	upper level - board - side 1	
5024-000-WD-006	6	Wood	upper level - board - side 2	
5024-000-WD-007	7	Wood	lower level support column for upper level near southwest entrance	
5024-000-WD-008	8	Wood	lower level near southwest entrance - board 1	
5024-000-WD-009	9	Wood	lower level near southwest entrance - board 2	
5024-000-WD-010	10	Wood	lower level near southwest entrance - board (rafter beam) - side 1	
5024-000-WD-011	11	Wood	lower level near southwest entrance - board (rafter beam) - side 2	
6709-17-WD-012	12	Wood	pre-drying rack room A	
6709-17-WD-013	13	Wood	pre-drying rack room A	
6709-17-WD-014	14	Wood	pre-drying rack room A	
6709-17-WD-015	15	Wood	pre-drying rack room B	
6709-17-WD-016	16	Wood	pre-drying rack room B	
6709-17-WD-017	17	Wood	pre-drying rack room B	
6709-17-WD-018	18	Wood	pre-drying rack room C	
6709-17-WD-019	19	Wood	pre-drying rack room C	
6709-17-WD-020	20	Wood	pre-drying rack room C	
6709-17-WD-021	21	Wood	was 1890-01-WD-021, pre-drying rack room C - surface covered with visible free propellant powder	
1890-01-WD-022	22	Wood	conveyor wooden support	see map
1890-01-WD-023	23	Wood	wall	see map
1890-01-WD-024	24	Wood	conveyor wooden support	see map
1890-01-WD-025	25	Wood	conveyor wooden support	see map
1890-01-WD-026	26	Wood	wall	see map
1890-01-WD-027	27	Wood	rack - top	see map
1890-01-WD-028	28	Wood	rack - bottom	see map
1890-01-WD-029	29	Wood	wall	see map
1890-01-WD-030	30	Wood	shelf	see map
9590-000-WD-031	31	Wood	east entrance tank support blocks (railroad tie - end)	
9590-000-WD-032	32	Wood	east entrance tank support blocks (railroad tie - side)	
5024-000-WD-033	33	Wood	composite of hot spots from upper level and one support beam lower level	

Table 2-2 Sampling Log Summary Table Continued				
Field Sample Identification #	**Map ID Number**	**Sample Matrix**	**Sample Description**	**Comments**
9590-000-CM-034	34	Concrete	Piece of loose concrete picked up from floor	
1885-01-CM-035	35	Concrete	concrete core sample	see map
1885-01-CM-036	36	Concrete	concrete core sample	see map
1885-01-CM-037	37	Concrete	concrete core sample	see map
1890-01B-CM-038	38	Concrete	concrete core sample	see map
1890-01B-CM-039	39	Concrete	concrete core sample	see map
1890-01B-CM-040	40	Concrete	concrete core sample	see map
1890-01B-CM-041	41	Concrete	concrete core sample	see map
1890-01B-CM-042	42	Concrete	concrete core sample	see map
1890-01B-CM-043	43	Concrete	concrete core sample	see map
1890-01B-CM-044	44	Concrete	concrete core sample	see map
1890-01B-CM-045	45	Concrete	concrete core sample	see map
1890-01B-CM-046	46	Concrete	concrete core sample	see map
1885-03S-CM-047	47	Concrete	concrete core sample	see map
1885-03S-CM-048	48	Concrete	concrete core sample	see map
1885-03S-CM-049	49	Concrete	concrete core sample	see map
1885-03S-CM-050	50	Concrete	concrete core sample	see map
1885-03-CM-051	51	Concrete	concrete core sample	see map
1885-03-CM-052	52	Concrete	concrete core sample	see map
1885-03-CM-053	53	Concrete	concrete core sample	see map
1885-03-CM-054	54	Concrete	concrete core sample	see map
1885-03-CM-055	55	Concrete	concrete core sample	see map
1885-03-CM-056	56	Concrete	concrete core sample	see map
1885-02-CM-057	57	Concrete	concrete core sample	see map
1885-02-CM-058	58	Concrete	concrete core sample	see map
1885-02-CM-059	59	Concrete	concrete core sample	see map
1885-02-CM-060	60	Concrete	concrete core sample	see map
1885-02-CM-061	61	Concrete	concrete core sample	see map
1885-02-CM-062	62	Concrete	concrete core sample	see map
1885-02-CM-063	63	Concrete	concrete core sample	see map
1885-02-CM-064	64	Concrete	concrete core sample	see map
1885-02-CM-065	65	Concrete	concrete core sample	see map
1885-02-CM-066	66	Concrete	concrete core sample	see map
1885-02-SS-067	67	Soil	surface soil sample, south end of bldg. foundation, exposed area near drain, just under concrete pad, 3' above ground	see map
1885-02-SS-068	68	Soil	surface soil sample, south end of bldg. foundation, exposed area near drain, just under concrete pad, 3' above ground	see map
1885-02-SS-069	69	Soil	surface soil sample, south end of bldg. foundation, exposed area near drain, just under concrete pad, 3' above ground	see map

Table 2-2 Sampling Log Summary Table Continued				
Field Sample Identification #	**Map ID Number**	**Sample Matrix**	**Sample Description**	**Comments**
1885-02-SS-070	70	Soil	surface soil sample, south end of bldg. foundation, exposed area near drain, just under concrete pad, 3' above ground	see map
1885-02-SS-071	71	Soil	surface soil sample, south end of bldg. foundation, exposed area near drain, just under concrete pad, 3' above ground	see map
1885-02-SS-072	72	Soil	surface soil separate hole dug near stake	see map
1885-02-SS-073	73	Soil	soil and debris from drain pipe at east (rear of building)	see map
1885-03-SS-074	74	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-03-SS-075	75	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-03-SS-076	76	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-03-SS-077	77	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-03-SS-078	78	Soil	composite subsurface soil sample from core holes 048 and 049	see map
1890-01B-SS-079	79	Soil	subsurface soil sample from hole where core sample was removed	see map
1890-01B-SS-080	80	Soil	subsurface soil sample from hole where core sample was removed	see map
1890-01B-SS-081	81	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-082	82	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-083	83	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-084	84	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-085	85	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-086	86	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-087	87	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-088	88	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-089	89	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-090	90	Soil	subsurface soil sample from hole where core sample was removed	see map

Table 2-2 Sampling Log Summary Table Continued				
Field Sample Identification #	**Map ID Number**	**Sample Matrix**	**Sample Description**	**Comments**
1885-02-SS-091	91	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-092	92	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-093	93	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-094	94	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-095	95	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-096	96	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-097	97	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-098	98	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-SS-099	99	Soil	subsurface soil sample from hole where core sample was removed	see map
1885-02-CM-100	100	Concrete	concrete core sample	see map
1885-02-CM-101	101	Concrete	concrete core sample	see map
1885-02-CM-102	102	Concrete	concrete core sample	see map
1885-02-CM-103	103	Concrete	concrete core sample	see map
EQ-RINSE 12/2/05	NA	Water	composite of concrete core equipment decon rinses	
EQ-RINSE 12/6/06	NA	Water	composite of concrete core equipment decon rinses	
EQ-RINSE 12/7/06	NA	Water	composite of concrete core equipment decon rinses	

WD= wood, SS= soil, CM= concrete material, EQ = equipment

2.4.2 Sample Collection

Sample collection methods varied with each matrix. The wood, soil and concrete matrices are described separately below. Sample locations were examined and swipe tested by the SUXOSO prior to sample collection to ensure the safety of the sampling crew.

Wood

Wood samples were generated using a cordless drill with a ¾" fluted bit. Wood sampling involved drilling multiple (35-50) holes to a depth of approximately one-half inch. Holes were placed close to each other, collecting the shavings on an aluminum foil lined tray. Single-use paint brushes were used to sweep errant wood shavings onto the foil-lined tray as necessary. The shavings were then transferred to a heavy duty Ziploc bag and were weighed on-location with a portable top-loading balance to ensure a sample size of at least 100 grams (g).

Concrete

Concrete samples were obtained using a remotely operated hydraulic drill. A water cooled, three inch (3") diameter diamond tipped hollow coring bit was used to drill completely through 6-8" concrete floor slabs. This allowed sampling of underlying soil at selected locations. All coring operations were performed under the supervision of a qualified unexploded ordinance (UXO) technician. The drill operator and the UXO technician controlled the drill from behind a blast shield placed a minimum of 250 feet from the coring site, and watched the progress of the drill using a remote camera.

Figure 2-7 Concrete Core Sampling Team

Core samples were taken at expansion joints between slab sections when possible, since these joints were expected to be likely pathways of contamination to underlying soil. Where cores were taken at expansion joints (Figure 2-8), the core was taken such that it included a portion of the expansion joint material, if possible. Though this material was not included in the list of matrices of the demonstration, swipe testing by the SUXOSO indicated that the joint compound might produce positive results. Samples were staged on aluminum foil and transferred to heavy duty Ziploc double bags.

Figure 2-8 Core Taken at Expansion Joint

Between 1 and 2 gallons of water per minute was applied to the drill location just enough to ensure that the bit remained well wetted for safety purposes. Water was discontinued as soon as the concrete slab was cored. Displacement of NC and NG was recognized as a possibility; however, for this demonstration, the water would most likely affect the total amount of NC and NG that may have been present (i.e. washed some away), but was unlikely to affect the ability to detect its presence, due to the insolubility of NC and NG in water. Determination of total quantities of NC and NG was not a primary goal of the demonstration, only the ability to provide a sample matrix for analytical method comparison. The impact on analysis was judged to be minimal when considering alternatives for safely obtaining samples for method testing.

Soil

Surface soil samples were taken by first loosening the soil with a one inch soil coring tool, then collecting the soil with a stainless steel (SS) spoon. Samples were staged on aluminum foil and transferred to trace-clean, 500ml amber, wide mouth glass sample jars. Figure 2-9 shows an example of soil sample location and conditions at the time of sampling.

Figure 2-9 Surface Soil Sample 1885-02-SS-0-72–Tunnel location Beside Bldg. 1885-02 Box Storage House

Sub-surface soil samples were taken from bore holes after concrete core samples were removed. Many of the sub-surface samples required thawing of the frozen ground before soil could be loosened and excavated from the holes. For samples requiring thawing, warm air of no higher than 140 degrees Fahrenheit was blown into each bore hole, soil was loosened using a SS auger, and soil was excavated using 16" SS spoon tongs. Samples were staged on aluminum foil or in heavy duty Ziploc bags and transferred to trace-clean, 500ml amber, wide mouth jars.

Samples of the expansion joint material were transferred to Ziploc bags, stored, and returned to the Knoxville Shaw Lab for subsequent testing.

Figure 2-10 Sub-Surface Soil-Bore Hole

Collection Equipment Decontamination

Decontamination of sampling equipment included rinsing drill bits, core sampler tongs and spoons with acetone and distilled water. Equipment rinse water composite samples were taken at various points during the concrete sample collection process (as listed in the Sampling Log Summary) and submitted to STL Sacramento for NC and NG analysis. In addition, brushes, aluminum foil and nitrile gloves were disposed of after each sample taken.

Sample Storage

Concrete core, wood shaving and soil samples used in the study were stored in an underground, explosion-proof bunker prior to analysis. The bunker temperature ranged from -10 to 20 degrees F (for the duration of on-site field testing) and was located approximately 100 yards from the field laboratory trailer. Samples transferred to the Shaw Lab in Knoxville were stored under refrigeration at 4°C.

2.4.3 Test Sample Preparation

Sample preparation methods included drying, crushing, grinding or chopping, sieving, and homogenization as needed per each matrix. The wood, soil and concrete matrices are described separately below.

Wood

Wood samples, as received, varied in consistency from fine chips or shavings (less than 1/8" thick) to four-inch splinters (thicker than ¼ inch) as shown in Figure 2-11. Samples were chopped intermittently for several minutes using a kitchen blender with a large capacity glass reservoir and stainless steel (SS) blades. Size reduction was deemed complete when the whole sample could pass through a ¼ inch sieve (Figure 2-12). Samples were further homogenized as needed, before taking aliquots, by stirring with a SS laboratory spatula. Sample preparation was performed in the field laboratory trailer's fume hood.

Figure 2-11 Nitrate House Wood Shavings from Transfer Trough Cover

Figure 2-12 Blender Homogenized Wood Less Than ¼ inch

Decontamination of preparation equipment included rinsing with acetone and distilled water, and blotting dry. In addition, aluminum foil and nitrile gloves were disposed of after each sample preparation was completed.

Concrete

Concrete core samples were screened for surface contamination using DROPEX^{Plus} prior to size reduction. Then core samples were prepared in a manner which maximized recovery of expected areas of contamination. This was accomplished by chipping away the top 1-1½ inch cross section and in some cases the side ½ inch longitudinal section next to the seam, if a seam existed. Large chips of concrete were crushed on a steel plate covered with Tyvek material using a hammer as shown in Figure 2-13. Size reduction was deemed complete when all particles were ¼ inch or less. Crushed concrete samples were transferred to Ziploc bags. Samples were further homogenized as needed before taking aliquots, by stirring with a SS laboratory spatula.

Figure 2-13 Crushing Concrete

Figure 2-14 Removal of Expansion Joint Material (EJM)

The expansion joint material (EJM) was removed from the concrete portion of the core and crushed with a hammer in the same manner as the concrete until particles were less than ¼ inch. The crushed EJM was then transferred to a plastic Ziploc bag and labeled using the concrete core sample number with an "EJM" appended. The joint material was a dried, tarry, rubber-like compound (Figure 2-14).

Concrete and EJM preparation was performed in the same bunker used for sample storage noted above. Because temperatures within the bunker ranged from minus10 to 0 degrees F, during the time when concrete was crushed, decontamination procedures were limited to replacing Tyvek material and carefully sweeping away residual dust particles between samples.

Analysis of the expansion joint material (EJM) was not included in the scope of work for the field demonstration. This material was sampled from 6 of the concrete cores and returned to the Shaw Knoxville lab for investigative analysis on this matrix. Results for the CRREL analysis of the EJM extracts are included in the CRREL concrete results section of the report.

Soil

Soil samples were air dried or oven dried at 40 degrees C as needed prior to sieving. Drying times varied greatly due to the moisture content of the samples. Some of the samples contained considerable amounts of moisture and rocks. Samples were mixed or shaken to loosen soil from rocks, sieved through a four (4) inch diameter SS hand strainer with ¼ inch openings, and collected on aluminum foil (Figure 2-15). Materials larger than ¼ inch were primarily rocks and were wasted. Soil samples were then spread thinly on foil and inspected closely for propellant material. Prepared soils were transferred to trace-clean, 500 milliliter (ml) amber, wide mouth glass jars. Small amounts of recovered propellants (Figure 2-16 and Figure 2-17) were removed from the soil samples, weighed, retained separately in 20 ml glass vials and submitted to the BAAAP UXO Officer for proper disposal. The solid propellant found in soil samples was not included for detection. Since the soil was being subsampled for field and reference lab analyses, there was no way to ensure that a solid piece could be appropriately portioned for each sample aliquot (obtain a homogeneous sample). Samples were further homogenized as needed before taking aliquots, by stirring with a SS laboratory spatula until visually homogenous.

Figure 2-15 Sieving Soil Samples

Figure 2-16 Propellant Removed from Soil Sample 1885-02-SS-073

Figure 2-17 Propellant Recovered from Soil Sample 1885-02-SS-072

Decontamination of sample preparation equipment between samples included rinsing with acetone and distilled water, and blotting dry. The hand strainer was obtained in kitchen supplies and was chosen to simplify decontamination between samples. In addition, aluminum foil and nitrile gloves were disposed of after each sample preparation was completed.

2.5 Sample Analysis Scheme

Three technologies for identifying and quantifying NC and NG in the field were evaluated on acetone extracts of wood, soil, and concrete material for comparison against off-site laboratory analysis. The methods evaluated were the following:

- DROPEX^{Plus} and EXPRAY™ colorimetric indicator for NC and NG,
- CRREL RDX colorimetric field screening method for NC and NG, and
- GC/TID portable field gas chromatograph for NG

Sample aliquots were weighed out from each of the prepared wood, concrete and soil samples into amber 4-ounce wide-mouth jars and labeled. Wood samples were weighed into 8-ounce jars due to the bulk size of the wood and to allow for mixing. An additional 20-gram aliquot of a sample was prepared for every 10 samples and analyzed as a field duplicate. Field duplicates were identified with the addition of an (A) to the respective sample number.

Acetone extracts were prepared of each concrete and soil sample using a 1:1 (v:w) ratio of acetone to sample material. Wood samples were extracted using a 3:1 ratio of acetone to wood material due to absorbtion characteristics of the pulverized wood. Extraction time was 1.5 hours for all three material types using a bench top shaker table on low speed. After extraction, the sample was allowed to settle prior to filtering. The extract was transferred to a 10-mL syringe, filtered into vials as shown in Figure 2-18, and stored at 4°C pending analysis.

Figure 2-18 Acetone Extracts of Soil Samples

Calibration standards and QC) samples were prepared and extracted along with the test samples from the clean homogenized background materials (wood, soil and concrete) prepared during the Shaw 2005 bench test. With each matrix extraction batch, or at a minimum of one every 20 samples, an extraction blank, laboratory control sample (LCS) and a matrix spike/matrix spike duplicate (MS/MSD) were prepared and extracted along with the test samples. A 10 milligram per milliliter (mg/ml) Nitroglycerine in methanol stock solution obtained from AccuStandard® was used for spiking NG standards/QC samples. A 4.2 mg/ml stock solution of NC in acetone prepared at the Shaw Lab from reference material 71% NC flake material (Lot 9H-9027, Hercules, Inc.) was used for preparing NC spiked material. Aqueous suspensions using NC were also prepared as described in the bench test (Shaw Bench Test, 2005) and used in spiking material for CRREL method tests.

Data obtained using the three field methods to analyze the prepared extracts is compared in the following sections with results from the conventional fixed-laboratory analyses of homogenous replicate sample splits submitted to STL Sacramento, CA. A split of each of the sample materials collected was packed into a cooler at 4°C and submitted to the off-site lab for quantitative analysis by the reference methods MCAWW 353.2 for NC and EPA SW-846 8330/8332 for NG.

Due to the extremely cold weather encountered during the demonstration, analytical problems, and time restraints all analysis could not be completed during the two week field demonstration. Test samples were returned to the Shaw Knoxville Lab to allow for completion and method development. Details of analytical problems encountered with NC analysis by the CRREL RDX method are discussed in the following field method sections per matrix.

2.6 Reference Test Methods

The reference methods SW-846 8330/8332 and MCAWW 353.2 are generally accepted to be the standard laboratory methods of analyses for NC and NG in homogeneous soil, water and sludge samples, but they were not developed nor thoroughly validated for the analysis of NC and/or NG in the sample matrices being tested at BAAAP. Any method may be affected by non-homogeneous matrices or matrix interferences, which cause poor sample extraction or inaccurate and imprecise analysis results, so comparison to the field methods may not be entirely appropriate for validation of the field methods. Nevertheless, it was not within the scope of this project to validate the reference methods, but to compare the field method performance to the results obtained by the reference methods.

Prior to the field demonstration as a part of the bench study samples of various substrates; soil, wallboard, wood and cement were spiked with various concentrations of NC, NG and a combination of NC and NG. The spiked samples were submitted to the STL outside laboratory for standard laboratory analysis using the reference methods. The resulting data was compared to the concentrations of the spike values added to the matrices for each analysis. The percent recovery for the reference methods are found along with the field method data in the Shaw Draft Bench Scale Report (Shaw, 2005). Percent recoveries varied between the different analyses and substrates, but in all cases with the exception of nitroglycerine in cement the analytes were detected, quantifiable and produced useable calibration curves for all of the sample matrices using the reference methods. The concentrations determined from the reference methods were plotted against the known spike concentrations to determine a calibration curve to compare verification/test samples using the reference and field methodologies.

Sample data obtained using the field methods on-site during the demonstration and subsequently at the Shaw Lab are compared in the following sections with results from the reference method analyses of homogenous replicate sample splits submitted to STL. Reference method data and data validation reports are included in Appendix B.2 and B.3, respectively, of this report.

2.6.1 Reference Method MCAWW 353.2 Methodology

MCAWW 353.2 method (EPA, 1983) is a colorimetric method that was used to determine nitrate, nitrite, each singularly, or a combination thereof. The method has been adapted for NC determination in the form of nitrate plus nitrite in waters, soils, and sediments. Solid samples are washed initially with methanol and water, agitated on a shaker, centrifuged, and then decanted. The residue is then extracted with acetone, agitated on a shaker, centrifuged, and decanted. The

acetone extracts are treated with sodium hydroxide and hydrolyzed. Once hydrolyzed, the extract is filtered, additional reagents are added for color development and analyzed colorimetrically on an automated colorimetric instrument.

The method is specific for the analysis of NC in a sample. The method pre-extraction steps with methanol and water remove inorganic forms of nitrate and nitrite as well as nitroglycerin from the sample. NC is insoluble in these solvents and is subsequently removed from the solid matrix in an acetone solvent extraction. The acetone extract is then hydrolyzed to remove NC compound nitro groups and produce inorganic nitrite and nitrate ions. The nitrate ions are then reduced to nitrite with a cadmium column and the total nitrite content is quantified colorimetrically after reaction with a reagent to produce a highly colored species that is a pink-red color.

2.6.2 Reference Method EPA SW-846 8330/8332 Methodology

EPA SW-846 Methods 8330/8332 (EPA, 1995/EPA, 1998) are high-performance liquid chromatography (HPLC) ultraviolet methods for the extraction and detection of explosive residues in waters, soils and sediments. Samples are analyzed on an HPLC with a reverse-phase column at an ultraviolet detection of 250 nanometers (nm). Solid samples are air-dried, ground, sieved through a 30-mesh screen, extracted with acetonitrile, treated with calcium chloride solution, filtered, and the extracts are analyzed by HPLC.

Results from the reference laboratory methods are incorporated into the appropriate sections below for comparison with the field method test results. Data validation reports are included in Appendix B.3.

3.0 FIELD TEST METHODS AND RESULTS

3.1 Qualitative Sample Screening Using DROPEX^{Plus} and EXPRAY™

3.1.1 Introduction/Narrative

DROPEX^{Plus} and EXPRAY™ colorimetric test kits were used to screen the prepared extracts of the collected site materials for the presence of NC and NG. Both test kits are designed to provide immediate detection of explosives (including NC and NG) by application of supplied reagents in a specified sequence. Qualitative screening using DROPEX^{Plus} was also performed by the field team at the time of sample collection to aid in the selection of the sample locations based on a positive indication of NC or NG contamination. Analyses were then performed at the field trailer on prepared sample extracts to give a qualitative indication of whether explosive compounds were present. Spiked reference materials prepared from the background soil, concrete and wood samples prepared during the bench testing were analyzed as control standards along with the test samples to obtain an indication of response for both NC and NG.

DROPEX^{Plus} wipe tests were also used to screen the surface of the concrete cores for explosive residue prior to crushing and pulverization. These results are included in the data table along with the extract results. DROPEX^{Plus}/EXPRAY™ was completed on 33 wood samples, 38 concrete samples, and 15 soil samples during the field demonstration. Due to time constraints, and frozen ground causing sampling problems 18 soil samples were returned to the Shaw Knoxville Lab for preparation and analysis.

3.1.2 Materials

DROPEX^{Plus} and EXPRAY™ colorimetric test kits were both purchased from Medimpex United, Inc. Both systems are based on the same reagents but are in different delivery form, i.e., spray can vs. dropper bottles. Each test kit is supplied with 2–inch-by-3-inch collection papers to perform the test. The kit wipes were used in the field during sample collection and to screen the concrete cores for surface contamination. For comparison purposes, the sample extracts were tested on Whatman No. 1 filter paper. An initial study was conducted during the bench scale testing to determine if a qualitative filter paper larger in size would provide the same reaction as the test kit paper and allow for testing multiple samples on the same test paper. A set of prepared NG standards were spotted on two different 15-cm Whatman filters, a Whatman No. 40 and a Whatman No. 1, and on the supplied DROPEX^{Plus}/EXPRAY™ paper. The test results showed that a Whatman No. 1 filter expressed the same sensitivity as the test kit and performing slightly better than the Whatman No. 40 paper. The larger test paper allows multiple samples from one test group to be tested side-by-side for ease of comparison and documentation of results. Figure 3-1 shows testing of sample extracts inside the field trailer.

Figure 3-1 Shaw Lab Trailer and EXPRAY™ Testing on DROPEX^{Plus} Sample Extracts

3.1.3 Method

Sample extracts were prepared using the procedure described in Section 2.5, Sample Analysis Scheme. Tests were performed using 10 micro liters (µLs) of extract placed onto the 15-cm filter paper using a 10-µL glass syringe and allowing it to air dry.

Using the EXPRAY™ kit the spray bottle labeled EXPRAY™ No. 1 was applied briefly at a distance of about 15 cm. The same area was then sprayed with the EXPRAY™ No. 2 can until slightly damp. In cases where NC or NG was detected, color change to pink or red was completed in seconds.

The DROPEX^{Plus} kit was tested identical to the EXPRAY™ using the same extracts. A couple of drops of Reagent No. 1 were spotted on the extract aliquot on the filter. Approximately 15 seconds later, a couple of drops of Reagent No. 2 were added.

If the test was positive for NC or NG, color change to red or pink was noted immediately as pictured in Figure 3-2.

Figure 3-2 Comparison of EXPRAY™ and DROPEX^{Plus} on BAAAP Wood Extracts

3.1.4 Data Assessment

For convenience, Table 3-2 provides a side by side comparison of the DROPEX^{Plus}/EXPRAY™ test kit results along with the off-site STL reference method results for each matrix tested. The DROPEX^{Plus}/EXPRAY™ results were recorded as either a positive (+) or negative (-) test response. In some cases, sample concentrations near the detectable limit for the method gave a positive result that was only faintly discernable, but in general, the test response was increasingly more intense as the test NC or NG concentration increased above the detectable limit. Detectable limits of spiked NC and NG material varied for each test matrix. Detection levels for each matrix were determined in the bench scale tests portion of this demonstration and are presented in Table 3-1 for reference. The qualitative response key used in the summary tables is as follows:

- = indistinguishable from blank

+- = possible detection

+ = detectable pink color

++ = darker pink-red color

+++ = red color

++++ = dark red

Table 3-1
Bench Test Detectable Limits DROPEX^{Plus}/EXPRAY™

Soil Extracts

Spike Material	EXPRAY™ Detectable Limit mg/kg	DROPEX^{Plus} Detectable Limit mg/kg
NC	250	100
NG	40	40
Combined NC/NG	250/25	250/25

Wood Extracts

Spike Material	EXPRAY™ Detectable Limit mg/kg	DROPEX^{Plus} Detectable Limit mg/kg
NC	2500	250
NG	250	80
Combined NC/NG	4000/400	250/400

Concrete Extracts

Spike Material	EXPRAY™ Detectable Limit mg/kg	DROPEX^{Plus} Detectable Limit mg/kg
NC	250	250
NG	ND	ND
Combined NC/NG	1000/100	250/25

NG – Nitroglycerine; NC – Nitrocellulose; mg/kg – milligrams per kilogram.

The performance of DROPEX^{Plus} and EXPRAY™ for identification of NC and/or NG compounds in acetone extracts of the wood, soil and concrete samples collected during the field demonstration was evaluated by comparison with the STL laboratory results. During the bench test both test kits seemed to work equally well and correlate well with the reference method, STL 8330/8332, with limitations based on detectable concentration limits for each matrix, which were matrix dependent. Findings from the bench test are included in the sections below for reference. Results obtained during the field demonstration by each test kit are evaluated for each of the three sample types tested in the sections below. Statistical analysis was applied to positive or

negative results from the field identification with the off-site STL lab results as reference. Test kit percent false negatives or false positives for each matrix are summarized in the tables below with the demonstration performance pass/fail criteria.

The demonstration field personnel preferred DROPEX^{Plus} during the sample collection screening due to the extremely cold temperatures (sub 0) at the BAAAP site in December. The Ex-pray spray cans did not perform as well in the extreme conditions encountered outdoors and were not used by the sample collection team. Results from the bench tests also indicated DROPEX^{Plus} test had lower detectable limits for NC spiked soil and wood, and for the combined NC and NG spiked samples of wood and concrete.

Wood

The DROPEX^{Plus} / EXPRAY™ ® detection levels described above were applied to the field demonstration samples. Table 3-2 shows the DROPEX^{Plus} / EXPRAY™ results for the 37 wood samples that were compared to the STL lab. The STL results indicate that all 37 wood samples had NC and/or NG present.

The false negative rate for the DROPEX^{Plus} analysis was 16.2 percent when compared with the laboratory reference methods. When looking at the false negative rate, it appears that DROPEX^{Plus} does not pass the performance metrics. However, when looking at the false positive rate of 5.4 percent, DROPEX^{Plus} passed the performance metrics. In certain situations DROPEX^{Plus} might still be used to indicate the presence of explosive compounds above the detectable level, given its low rate of false positives. Fifty percent, or 3 out of six of the false negative results showed possible detection but not conclusive (+-), these results were treated as non-detect for data comparison purposes.

The false negative rate for the EXPRAY™ analysis was 0 percent when compared with the laboratory reference methods and passes the performance metrics. However, when looking at the false positive rate of 13.5 percent, EXPRAY™ does not pass the performance metrics. In certain situations DROPEX^{Plus} might still be used to indicate the lack of explosive compounds above the detectable level, given its low rate of false negatives. The lack of false negatives and high percent of false positives for EXPRAY™ was most likely due to the higher detection level (2500 mg/kg) for this test kit. The detection limits for Drop-Ex and Expray were defined in the bench testing portion of the demonstration on spiked homogenized sample matrix. The concentrations used in the test were 0, 2.5, 10, 80, 250, 2500 mg/kg NC on wood and the detection limit was based on the first level with a clear positive indication, which was 2500 mg/kg; however, additional standards at levels between 250 mg/kg and 2500 mg/kg may have been able to better define the detection level. In the field demonstration, samples were chopped and mixed as much as possible to obtain homogeneous media; however, it is believed there was still a considerable amount of non-homogeneity. This was probably due to the inability to chop and blend contaminated surface pieces into the bulk sample to the level necessary. As a result NC was detected by Expray on a sample with a concentration of 138 mg/kg by the reference method, but also NC was not detected on a sample with an NC concentration of 1020 mg/kg. It is believed that the discrepancy was due primarily to sample non-homogeneity.

Table 3-2 DROPEX^{Plus} / EXPRAY™ Wood Results

Sample Identification	STL Reference Method Results (mg/kg)		Drop-Ex	Expray
	Method 8330 NG	Method 353.2 NC	Extract (10 uls)	Extract (10 uls)
6657-02N-WD-001	3.7	190	-	-
6657-02N-WD-002	18	851	-	-
6657-02I-WD-003	ND<0.5	39.9	-	-
6657-02I-WD-003A	ND<5	43.2	-	-
6657-02I-WD-004	ND<0.5	1020	-	-
5024-000-WD-005	ND<5	221	+	-
5024-000-WD-006	ND<5	174	+	-
5024-000-WD-007	ND<5	697	+	-
5024-000-WD-008	ND<5	40.5	-	-
5024-000-WD-009	ND<0.5	44.6	-	-
5024-000-WD-010	ND<5	332	++	++
5024-000-WD-011	ND<2.5	138	+	+
6709-17-WD-012	99	143	+-	-
6709-17-WD-013	88	115	+	-
6709-17-WD-014	230	198	+	+
6709-17-WD-015	240	198	+	++
6709-17-WD-016	180	156	+-	-
6709-17-WD-017	130	172	+-	-
6709-17-WD-018	84	122	+	-
6709-17-WD-019	120	149	+	-
6709-17-WD-020	110	96.2	+	-
6709-17-WD-020A	120	113	+	-
6709-17-WD-021	62	286	++	++
1890-01-WD-022	ND<0.5	35.3	+-	-
1890-01-WD-023	ND<0.5	19.1	-	-
1890-01-WD-024	ND<0.5	27.6	-	-
1890-01-WD-025	ND<0.5	61.8	+-	-
1890-01-WD-026	ND<0.5	19.8	-	-
1890-01-WD-027	ND<5	46.3	+	-
1890-01-WD-028	ND<5	29.1	-	-
1890-01-WD-028A	ND<5	42.4	-	-
1890-01-WD-029	ND<5	56.5	-	-
1890-01-WD-030	ND<5	46.6	+-	-
9590-000-WD-031	ND<0.5	42.9	+	-
9590-000-WD-032	ND<10	54.8	-	-
5024-000-WD-033	ND<0.5	2880	+++	+++
5024-000-WD-033A	ND<0.5	7080	+++	+++

ND = Not detected at the specified method detrection limit
NA = Not analyzed or not applicable
+ = Detected
- = Not detected
+- = Possible detection; slight coloration, but difference from blank color was inconclusive

Soil

The DROPEX^{Plus}/ EXPRAY™ detection levels described above were applied to the field demonstration samples. Table 3-3 shows the DROPEX^{Plus} / EXPRAY™ results for the 37 soil samples that were compared to the offsite STL lab. These results indicate that all 37 soil samples had NC and/or NG present.

Of the 37 results for soil samples tested using DROPEX^{Plus} there were (6) or 16.2 percent false positives and 10.8 percent false negative results. Three of the 6 false positive results were very near the 100 mg/kg detectable level for NC on soil. The results from the reference method 8330 were very low for NG with values ranging from ND to 3.0 mg/kg. Since the lowest detectable level for NG by DROPEX^{Plus}/EXPRAY™ is 40 mg/kg only NC could be evaluated for false positives, however DROPEX^{Plus} does not meet the performance metrics for false positives or false negatives on soil extracts.

EXPRAY™ analysis gave a false negative rate of 2.7 percent with 8.1 percent false positives when compared with the laboratory reference methods. EXPRAY™ does not meet the performance metrics criteria for < 5 percent false positives.

Concrete Material

Concrete Core Sample Pre-analysis Screens (DROPEX^{Plus})

Concrete samples were screened for the presence of NC and NG prior to extraction and analysis of the extracts. Samples were screened using the DROPEX^{Plus} test kit on wipes of sample surfaces. Concrete cores were wiped on the top-end exposed surface and the bottom-end or ground side surface. If the core had exposed crack or expansion joint material surfaces, they were wiped and tested. One sample, sample 9590-000-CM-034, was composed of a number of surface chips each approximately three quarters of an inch or less in thickness. The upper surface of a number of the chips in the sample were wiped and tested using the DROPEX^{Plus} test. Sample 1885-03-CM-055 was stuck in the core drill bit and was overlooked during sample screening. After removal from the bit it was crushed for extraction without being screened, so screen results are not available for this sample. The results from the surface wipe tests are included with the sample extract results in summary Table 3-4 below.

The surface wipe test produced more positive results for the indication of NC/NG than either the DROPEX^{Plus} test or EXPRAY™ test on sample extracts. This suggests that contamination was more concentrated on the concrete surface rather than being predominantly incorporated into the bulk material. There were ten (10) samples with positive wipe indications for NC/NG as compared to only two (2) sample extracts with positive DROPEX^{Plus} indications as described below. Wipe tests on core crack surfaces or surfaces against expansion joint material typically gave similar NC/NG indication as that obtained for the top-end exposed surface. In most cases the wipes of core bottom-end surfaces gave similar NC/NG indication as that obtained for the top-end exposed surfaces.

Concrete Material Extracts

The DROPEX^{Plus}/ EXPRAY™ detection levels described above were applied to the field demonstration samples and evaluated. Table 3-4 shows the DROPEX^{Plus}/ EXPRAY™ results for the 41 concrete samples that were compared to the offsite lab. The reference method results indicate that all 41 concrete samples had NC present while only 1 sample contained NG above the reporting limit.

Table 3-3 DROPEX^{Plus} / EXPRAY™ Soil Results

Sample Identification	STL Reference Method Results (mg/kg)		Drop-Ex	Expray
	Method 8330 NG	Method 353.2 NC	Extract (10 uls)	Extract (10 uls)
1885-02-SS-067	ND<0.5	203	+	+
1885-02-SS-068	0.55	551	++	++
1885-02-SS-069	0.36	400	++	+
1885-02-SS-070	ND<0.5	57.6	++	+
1885-02-SS-071	ND<0.5	11.2	-	-
1885-02-SS-072	2.1	6200	+++	++
1885-02-SS-072A	1.4	6640	++++	+++
1885-02-SS-073	ND<0.5	11.8	+	-
1885-03-SS-074	ND<0.5	2.5	-	-
1885-03-SS-075	ND<0.5	39.6	-	-
1885-03-SS-076	ND<0.5	51.3	+-	-
1885-03-SS-077	ND<0.5	15.0	-	-
1885-03-SS-078	ND<0.5	31.4	-	-
1890-01B-SS-079	ND<0.5	3.2	-	-
1890-01B-SS-080	0.55	182	+	+
1890-01B-SS-081	ND<0.5	11.6	+	+-
1890-01B-SS-081A	ND<0.5	39.5	-	-
1890-01B-SS-081B	NA	NA	NA	NA
1890-01B-SS-081C	NA	NA	NA	NA
1885-02-SS-082	1.0	1970	+	++
1885-02-SS-083	3.0	275	+	++
1885-02-SS-083A	ND<0.5	431	+	+
1885-02-SS-084	ND<0.5	234	+	+
1885-02-SS-085	0.19	174	+	+
1885-02-SS-086	ND<0.5	21.4	+-	-
1885-02-SS-087	0.82	558	+	+
1885-02-SS-088	0.39	11.2	-	-
1885-02-SS-089	ND<0.5	24.4	-	-
1885-02-SS-090	ND<0.5	2.8	-	-
1885-02-SS-091	ND<0.5	266	+	+
1885-02-SS-092	ND<0.5	37.4	+	+-
1885-02-SS-093	0.18	340	-	-
1885-02-SS-093A	ND<0.5	92.2	-	-
1885-02-SS-094	ND<0.5	9.9	-	-
1885-02-SS-095	ND<0.5	66.8	+-	+
1885-02-SS-096	ND<0.5	2.3	-	-
1885-02-SS-097	ND<0.5	87.9	+-	-
1885-02-SS-098	ND<0.5	55.7	++	+
1885-02-SS-099	ND<0.5	62.5	+	+-

ND = Not detected at the specified method detrection limit
NA = Not analyzed or not applicable
+ = Detected
- = Not detected
+- = Possible detection; slight coloration, but difference from blank color was inconclusive

Table 3-4 DROPEX^{Plus} / EXPRAY™ Concrete Material Results

	STL Reference Method Results (mg/kg)		Core Surface Wipes Drop-Ex Test			Drop-Ex	Expray
Sample Identification	Method 8330 NG	Method 353.2 NC	Top	Bottom	Crack	Extract (10 uls)	Extract (10 uls)
9590-000-CM-034	ND<0.5	201Q	++	-	-	-	-
9590-000-CM-034A	ND<0.5	63.0	++	NA	NA	-	-
1885-01-CM-035	ND<0.5	17.1	+	+	NA	+-	-
1885-01-CM-035B	NA	NA	NA	+	NA	+-	-
1885-01-CM-036	ND<0.5	20.3	+-	+-	NA	-	-
1885-01-CM-037	ND<0.5	17.9	+	+	NA	-	-
1890-01B-CM-038	ND<0.5	5.7	-	-	NA	-	-
1890-01B-CM-039	ND<0.5	30.1	+	+	NA	-	-
1890-01B-CM-040	ND<0.5	17.8	+	+	NA	-	-
1890-01B-CM-041	ND<0.5	9.9	+	+	NA	-	-
1890-01B-CM-042	ND<0.5	95.9Q	+	+	NA	-	-
1890-01B-CM-043	ND<0.5	71.9Q	++	+	++	-	-
1890-01B-CM-043A	ND<0.5	36.8	NA	NA	NA	-	-
1890-01B-CM-044	ND<0.5	10.2	-	-	NA	-	-
1890-01B-CM-045	0.23J	87.8Q	-	-	NA	-	-
1890-01B-CM-046	1.1	261Q	++	++	NA	+	-
1890-01B-CM-046A	0.46J	42.7	NA	NA	NA	+	-
1885-03S-CM-047	ND<0.5	3.1JB	-	-	-	-	-
1885-03S-CM-048	ND<0.5	3.0JM	-	-	NA	-	-
1885-03S-CM-049	ND<0.5	6.8JM	-	-	NA	-	-
1885-03S-CM-050	ND<0.5	3.4JM	-	-	NA	-	-
1885-03-CM-051	ND<0.5	3.2JM	-	-	NA	-	-
1885-03-CM-052	ND<0.5	5.3JM	-	-	NA	-	-
1885-03-CM-053	ND<0.5	8.8JM	-	-	NA	-	-
1885-03-CM-054	ND<0.5	5.0JM	-	-	NA	-	-
1885-03-CM-055	ND<0.5	4.0JM	NA	NA	NA	-	-
1885-03-CM-056	ND<0.5	9.8JM	+-	NA	+-	-	-
1885-02-CM-057	ND<0.5	36.1JM	-	-	NA	-	-
1885-02-CM-058	ND<0.5	3.1JM	-	NA	NA	-	-
1885-02-CM-059	ND<0.5	6.1JM	-	-	NA	-	-
1885-02-CM-060	ND<0.5	8.7JM	-	-	NA	-	-
1885-02-CM-061	ND<0.5	9.8JM	-	NA	+-	-	-
1885-02-CM-062	ND<0.5	7.3JM	-	-	NA	-	-
1885-02-CM-063	ND<0.5	11.5JM	-	-	NA	-	-
1885-02-CM-064	ND<0.5	4.2JM	+-	+-	NA	-	-
1885-02-CM-065	ND<0.5	6.9JM	-	-	NA	-	-
1885-02-CM-066	ND<0.5	7.6JM	-	-	NA	-	-
1885-02-CM-100	ND<0.5	3.5JB,JM	+	-	NA	-	-
1885-02-CM-100A	ND<0.5	4.4JB,JM	NA	NA	NA	-	-
1885-02-CM-100B	NA	NA	NA	NA	NA	-	-
1885-02-CM-101	ND<0.5	2.2JB,JM	-	-	NA	-	-
1885-02-CM-102	ND<0.5	3.4JM,JB	-	-	NA	-	-
1885-02-CM-103	ND<0.5	3.5JM,JB	-	NA	+-	-	-

Q= Elevated reporting Limit
J = Estimated result. Result is less than reporting limits.
JS = Estimated result. Surrogate recovery is outside stated control limits and reanalysis was outside hold time.
JM = Estimated result. MS/MSD recovery is outside stated control limits.
JB = Estimated result. Method blank contains contamination.
ND = Not detected at the specified method detrection limit
NA = Not analyzed or not applicable
+ = Detected
- = Not detected
+- = Possible detection; slight coloration, but difference from blank color was inconclusive

For the 41 results for concrete samples tested DROPEX^{Plus} had 2.4 percent false positives and 2.4 percent false negative results. DROPEX^{Plus} does meet the performance metrics for false positives and false negatives on concrete extracts.

EXPRAY™ ® analysis gave a false positive rate of 0 percent with 4.9 percent false negatives when compared with the laboratory reference methods. EXPRAY™ meets the performance metrics criteria of less than 5 percent (<5%) percent false positives and less than 10 percent (<10%) false negatives.

3.1.5 Data Assessment Summary

Performance metrics for each sample group are summarized in Table 3-5 below. EXPRAY™ on wood and concrete and DROPEX^{Plus} on concrete extracts all pass performance criteria within matrix dependent detection limitations. Values meeting the specified demonstration performance metrics are bolded in the table.

Table 3-5 DROPEX^{Plus} / EXPRAY™ Summary of Performance Measures

Sample Type		Wood		Soil		Concrete	
Performance Measure	Pass/Fail Criteria	DROPEX	EXPRAY	DROPEX	EXPRAY	DROPEX	EXPRAY
% False Positives	NMT 5%	**5.4**	13.5	16.2	8.1	**2.4**	**0.0**
%False Negatives	NMT 10%	16.2	**0.0**	10.8	**2.7**	**2.4**	**4.9**
%Combined False Positive/Negative	NMT 15%	21.6	**13.5**	27.0	**10.8**	**4.8**	**4.9**
Total# Samples Evaluated		37	37	37	37	41	41

NMT= not more than

3.1.6 Conclusion

- DROPEX^{Plus} analysis of concrete core samples by surface wipes yielded more positive results (10 positives) than the sample extract analyses (2 positives) and suggested

increased sensitivity was observed because contamination was concentrated on the sample surface.

- EXPRAY™ was effective in detecting NC and NG in the matrices with results consistent with the STL 8330/8332 reference method as long as concentrations were above detectable limits.

- DROPEX^{Plus} did not meet the performance metrics for wood or soil and this was likely due to lower detection limits, which involved more samples with concentrations near the detection limit where variability in method performance is the highest and has the greatest impact.

- NG was detected on three samples in the cement matrix at very low levels (45, 46, 46A) This is believed to be due to hydrolysis degradation caused by the alkaline nature of the matrix. After applying the bench scale response curve to the STL data (see discussion in Section 3.2.4), NC was detected above the 250 mg/kg detection level for DROPEX^{Plus}/EXPRAY™ on two samples (34, 46) by the reference method. The low value for percent false positive/false negative is largely influenced by the lack of significant quantities of energetic materials in this matrix.

- Detectable limits were affected by the ratio of solvent to sample that was necessary to get complete matrix wetting for extraction. Wood matrix required a 3:1 ratio of acetone volume to sample weight. For soil and cement, a ratio of 1:1 was used.

- During Bench scale tests three false negatives were obtained (one EXPRAY™ and two DROPEX^{Plus}) out of a possible 91 tests that had concentrations above the detectable limits. The detectable limits were defined as the lowest concentration detected for each matrix. The three false negatives were for tests with concentrations just above the lowest detectable concentration observed for the matrix, and the test responses were faint near the detectable limit.

- EXPRAY™ tests, while slightly less sensitive, was easier to evaluate as either detect or non-detect. This can be seen in figure 3-2 above. DROPEX^{Plus} when applied seemed to spread out more and had more prevalent yellow discoloration. With both applications only an immediate and distinct color change should be considered to be a positive result. If the collection paper is left exposed, once reagents have been applied, it is possible for a color change to occur after a given amount of time due to pollutants or contaminants present in the ambient air.

- Both the EXPRAY™ and DROPEX^{Plus} field kits are easy to use with little specialized training and equipment. Each kit contains reagents for 200 tests. Cost of each EXPRAY™ kit is $240 and contains reagents for 100 tests. Cost of each DROPEX^{Plus} kit is $190 and contains reagents for 50 tests.

- Overall EXPRAY™ / DROPEX^{Plus} is thought to be a useful tool for screening the presence of significant concentrations of NC and or NG in the field or on sample extracts. Given its relatively low rate of false negative results, in combination with other field methods it could be a beneficial screening tool for identifying areas that do not contain explosive contamination in buildings within specified limits. Detectable levels are matrix dependent, with low confidence in results at or near the detection

limit. The field method should only be used as a screening tool in combination with other supportive methods of analysis.

3.2 Quantitative Analysis Using CRREL RDX Method

3.2.1 Introduction/Narrative

Samples were analyzed for NC and NG based on CRREL RDX Method (SW-846 Method) 8510 "Colorimetric Screening Procedure for RDX and HMX in Soil" (EPA, 2000). The CRREL RDX method is a non specific method for analysis of RDX and HMX, but it also provides response for chemically related organonitrate esters such as NC and NG. It has been used for these analytes in previous testing (Stone & Webster, 2003 and Shaw, Bench Scale Test, 2005). The method is a colorimetric procedure for the determination of nitrite released from the NC and NG propellant compounds. Matrix specific calibration on wood, soil and concrete was performed for each analyte using clean matrix material from the site, which was used in the previous bench test (Shaw, Bench Scale Test, 2005). Results were obtained for the total of NC and NG in terms of either NC or NG depending upon whether the calibration for NC or NG was used, respectively. Generating a calibration curve using both NC and NG combined was not practicable, due to the infinite number of ratios between NC relative to NG or NG relative to NC that may be encountered during analysis.

3.2.2 Instrumentation and Materials

Colorimetric analyses were performed using a HACH DR/2010 spectrophotometer set in the absorbance mode at 507 nanometers (nm). Sample extracts were filtered and treated using method procedures and then transferred into 25-mL glass cuvettes for absorbance measurement. Other critical materials used in the analysis are listed below.

Zn dust:	Zinc, 325-mesh (Aldrich catalog # 20,998-8)
Ion exchange resin:	Alumin-A, 3-mL (Supelclean, Supelco 5-7082)
Filters:	0.45 µm syringe filters (Acrodisc, 25 mm)
Nitrite color development reagent:	NitriVer 3 powder pillow, 25-mL (Hach Company)
Acetic acid	Glacial acetic acid, J.T. Baker, Baker Instra-Analyzed Reagent, 99.9%.
Sodium hydroxide	Aqueous sodium hydroxide solution, Ricca Chemical Company, 50% (w/w) aqueous solution, Lot# 2112341

3.2.3 CRREL Methodology

Aliquots of sample extracts for analysis were obtained as described in Section 2.5, Sample Analysis. This extraction method was somewhat different than that used in the bench tests for the CRREL method, but was used so that a single sample extraction would provide extract for analysis by all procedures rather than having to do separate extractions for each procedure. In the bench tests the acetone extractant volume to solid sample ratio was 5:1 (v/w). In these tests the ratio was decreased to 1:1 for soil and concrete matrices and 3:1 for wood samples. The decrease in extractant volume offered the potential for an increase in method sensitivity/decrease in detection limits.

The CRREL method steps for analysis of NC and NG in the sample matrices comprise the following:

1. Extraction of NC and NG from the solid matrix into acetone solvent
2. Filtering of the acetone extract to remove particulate and passing the extract through an alumina ion exchange resin to remove free nitrate and nitrite (inorganic forms)
3. Hydrolysis of NC and NG to remove nitro groups from the analytes and produce free nitrite and nitrate ions
4. Reduction of the free nitrate to nitrite ions
5. Reaction of the free nitrite ions with a coloring agent to produce a characteristic colored solution for quantitative determination.

The ion exchange resin used to remove inorganic nitrites/nitrates was a Supelco Alumin-A disposable resin column. Sample extracts were pushed through the resin column using a syringe at a rate of approximately one milliliter per minute. The CRREL RDX method hydrolysis step was performed under acid conditions using acetic acid and nitrate reduction to nitrite was performed with zinc dust. The color for absorbance measurement was developed by adding the contents of a HACH NitriVer 3 powder pillow dissolved in deionized water to the zinc reacted solution. After a minimum of 90 minutes, the color was developed, the sample was transferred to a 30cc syringe and filtered into a 25-mL cuvette and absorbance read at 507 nanometers (nm). A pink to rose color was indicative of NC/NG. See Figure 3-3.

Figure 3-3. CRREL Method Color Development

3.2.4 Data Assessment

Method Quantification and Data Treatment

Sample concentrations were quantified using the method by comparing sample color responses to those for matrix specific standards. Matrix standards were prepared separately for NC and NG by spiking blank matrix from the bench tests with standard NC or NG solutions as described in Section 2.5, Sample Analysis. Calibration curves were developed for each matrix to correct for matrix influences on the analysis method. New curves from those used in the bench tests were prepared primarily due to changes in extraction procedures as previously described. The calibration curve was checked at a minimum before and after sample analyses by reading control standard test samples to verify instrument response within 25 percent of the expected value.

During the field demonstration matrix effects prevented the ability to obtain a usable calibration curve for NC in wood. Due to time constraints the wood extracts were returned to the Shaw Lab for further method development and optimization. As a result of this, a Shaw Modified CRREL Method for NC and NG detection was developed which improved the NC response for all matrices tested. Details of these developments and method results are described in the following sections.

For the STL reference methods, MCAWW 353.2 and SW-846 8330, the results for the analysis of samples were reported by STL as absolute concentrations that were determined from the analysis of standard calibration solutions. The results from STL analyses have been corrected for matrix effects based on results obtained in the bench test for spiked matrix calibration

samples. Except for the concrete matrix the STL results for NG by Method 8330 were within 10 percent and results were not corrected. The NG results on concrete from the bench test were significantly affected by the matrix, which is believed to be due to decomposition because of the alkaline nature of concrete. Because the nature of this effect is dynamic, and the NG results were typically low in comparison to NC, the STL results for NG on concrete samples were also not corrected. The STL MCAWW 353.2 results for NC on wood, soil and concrete have been corrected for comparison to CRREL method results and the corrections were similar for the three matrices resulting in an increase in value by a factor of 1.5 to 2. Also, since the CRREL method is a total analysis method for NC and NG, for comparison with STL results the STL NG specific result by Method 8330 and the corrected NC specific result by MCAWW 353.2 were totaled for each sample.

Method Detection and Comparison

The detection limit for the CRREL field methods was set as the value for the lowest standard used in the matrix calibration curve. Detection of NC/NG by the CRREL method was indicated as a "1" for values above the NC detection limit and a "0" for non-detect (ND) results. The NC detection limit was used as a conservative measurement because it was less sensitive than NG. In addition, there were no samples analyzed containing detectable levels of NG that did not contain detectable amounts of NC and they were typically substantially higher than the NG amounts.

Total NC/NG analyte detection for the STL reference methods was indicated for NC values above the MCAWW 353.2 method detection limit for the same reasons described above for the CRREL methods. In fact, there were no STL "non-detects" for NC/NG because NC was detected in all samples by the MCAWW 353.2 method. However, for comparison of the CRREL field methods with the STL reference methods the total of the STL Method 8330 NG result and the corrected STL MCAWW 353.2 result was also screened against the appropriate CRREL method detection limit. STL total values above the CRREL method detection limit were indicated as "detects" and each was given a value of "1" and values below were designated as "non-detects" and given values of "0." The sum of detects for analysis of samples by a method was the total of positive results by the method. The difference in detection between the STL methods and the CRREL methods was quantified by subtracting the detect value for the CRREL method from the STL methods detect value (using the CRREL detection limit screened detect value). Zero difference values indicated method agreement, -1 value was designated as "false positives" and +1 values were designated as "false negatives." The percentage of false positives and false negatives were calculated from these numbers.

Quantitative Method Comparison

To quantitatively compare CRREL method results to the STL totaled NG and corrected NC results the relative percent difference (RPD) between the two results for each sample was calculated. The result difference was taken as the total STL value minus the CRREL result, so a positive difference indicated a lower value was obtained for the CRREL method relative to the STL total result and a negative difference indicated the CRREL method gave a higher value. Non-detect (ND) results were set at the detection limit for this comparison except when non-detects were obtained for both methods and the non-detect levels were not similar. In this case the sample results were not included in the comparison analysis. If a positive result by one method was significantly lower than a non-detect level in the other method, these results were also excluded from the comparison analysis. The average RPD for the qualified data set was calculated and this metric indicated the bias of the CRREL results relative to the STL total

results as described. The standard deviation of the sample RPD data set was also calculated and this indicated the degree of scatter in the method agreement. The average RPD for the data set was also used to calculate the average ratio of CRREL result value to STL result value and this was expressed as a percentage.

In addition, a correlation plot of field method (CRREL) results to STL reference method results was prepared and the ideal 1:1 data line was shown. This helped to visualize result bias and scatter in method agreement. A linear regression of the results was also performed as a further metric of agreement between method results. A linear regression R^2 value of 0.95 or greater was defined as one criterion for method agreement. In some cases where results were obtained over several orders of magnitude logarithmic scales were used on the plots and linear regression results were not linear on the plots. In these cases it was found that plotting the line represented by the average RPD obtained between the CRREL and STL results provided a usable visual indicator for the central tendency of the CRREL data.

3.2.5 Wood

Calibration and Method Development

Analysis of NG spiked wood samples in the field by the CRREL RDX method did produce a response consistent with the bench test results that would allow calibration and sample analysis. However, initial attempts at analysis of NC spiked wood standards in the field with the CRREL RDX method did not yield a response even at a high concentration of 6,000 mg/kg. Sample analyses were delayed until method development at the Shaw Lab in Knoxville, TN was able to modify the procedure to obtain usable results for both NC and NG. Sample extracts that were returned from the field were analyzed at the Shaw Lab by the Shaw Modified CRREL procedure for NC/NG.

Method development at the Shaw Lab focused on determining which step or steps in the CRREL procedure was or were being interfered with by the wood matrix during NC analysis. Dilutions of wood matrix standards failed to produce a usable response for NC, so the matrix effect could not be diluted out even to obtain results with an elevated detection limit. Analyses of extracts of clean wood matrix spiked with NC also did not give an NC response, which suggested that the interference was likely due to something other than the failure to extract NC from the wood matrix. Subsequent analyses of clean wood extracts spiked with nitrite ion and nitrate ion produced very strong responses and these results indicated that the nitrate ion reduction step and the reagent color development steps were not being interfered with by the matrix. The cumulative results pointed to the acid hydrolysis step as the one being interfered with by the wood matrix. An increase in the amount of acetic acid and extension of the hydrolysis reaction time was tested for improvement but neither provided a significant impact, so alkaline hydrolysis using sodium hydroxide was investigated. Alkaline hydrolysis of NC and NG is used in the STL reference method (MCAWW 353.2). To modify the CRREL RDX method for alkaline hydrolysis the amount of sodium hydroxide had to be small so that addition of a minimum amount of acetic acid could re-establish an acidic pH for the Zn reduction and color development steps. This was accomplished in the test by using 0.1 mL (100 microliters) of 50 percent sodium hydroxide for hydrolysis of 5 mL of sample extract followed by addition of 0.5 mL of acetic acid. The hydrolysis step included mixing the sample extract with the sodium hydroxide for two minutes before adding the acetic acid. Tests were also performed to optimize the Zn reduction reaction time for NC and NG by this procedure and this was determined to be 15 to 30 seconds. Alkaline hydrolysis by this procedure provided a much better response for NC in wood extract than what was previously obtained for NC using the CRREL RDX method for any matrix. The

wood matrix did not interfere significantly with the NC response when the acetone extract volume to matrix ratio of 9:1 (v/w) was tested. At a lower solvent to wood ratio of 3:1 the more concentrated wood matrix extract did interfere by suppressing the NC response. Based on these results a Modified CRREL method was used to analyze the wood samples. This method used a 3:1 dilution of the wood sample extract with acetone. The wood sample extractions were performed at a solvent to wood ratio of 3:1, so a further 3:1 dilution provided an extract at a concentration equivalent to a 9:1 extraction ratio. The extract was then treated with alkaline hydrolysis and acidified by addition of acetic acid as described. The Zn reduction and color development steps were then performed per the CRREL method.

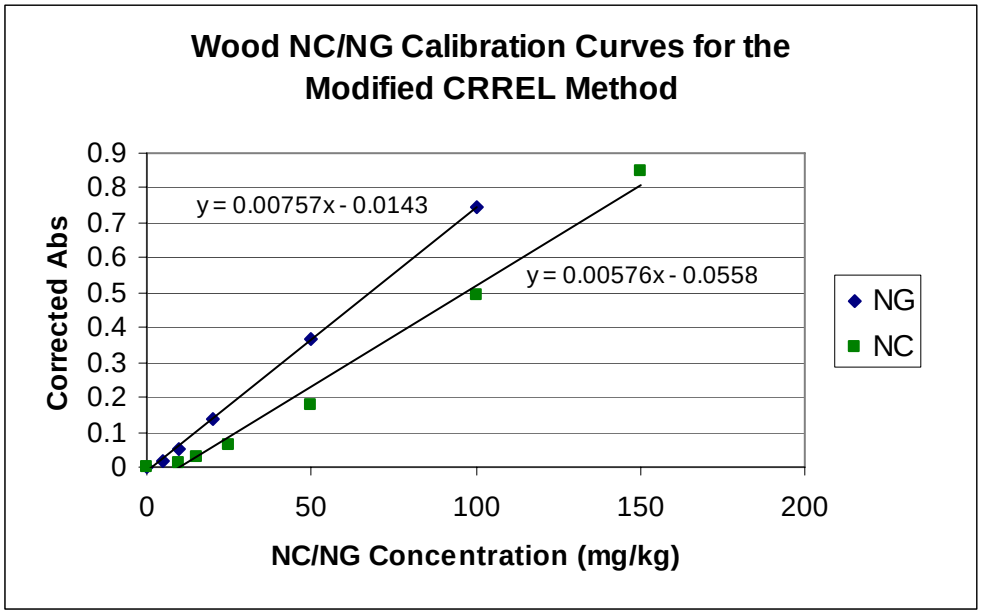
A calibration curve for NC in wood using the CRREL RDX procedure was obtained in the bench tests, but only at high concentrations and Table 3-6 shows a comparison of the standard concentrations and method responses with those from the Modified CRREL procedure. The data show that the response for NC by the modified method is on the order of a hundred times greater than the CRREL RDX method and suggests that the CRREL RDX procedure on wood extracts converts less than one or two percent of the NC nitrogen (N) to nitrite for analysis. The increase in response for NC is seen on other matrices as well and suggests the degree of N conversion to nitrite from NC is incomplete for the CRREL RDX procedure or is easily interfered with by sample matrices.

Table 3-6 Comparison of CRREL Method Calibration Results for Wood

CRREL RDX Method Bench Scale Wood Calibration Sample Analyses		**Shaw Modified CRREL NC/NG Method Field Demonstration Wood Calibration Sample Analyses**	
mg/kg NC	Absorbance	mg/kg NC	Absorbance
20	0.001	10	0.017
50	0.003	15	0.029
100	0.001	25	0.068
400	0.000	50	0.183
4000	0.080	100	0.498
40000	0.209	150	0.850

For NG a separate calibration curve was generated using the background materials prepared during the bench scale test. Five NG-spiked wood samples (calibration samples) were prepared and analyzed by the CRREL RDX method. Absorbance responses for NG were found to be linear and similar to those obtained for NC as shown in Figure 3-4. The calibration response for NG was 1.31 times that of NC, which is exactly the expected theoretical ratio based on the ratio of N content of NG (molecular fraction of N, $f_N = 0.185$) to the N content of completely nitrated NC ($f_N = 0.141$). The f_N ratio of NG to NC is 0.185/0.141 = 1.31. The similarity of NC and NG responses was not observed with the CRREL RDX method in the bench test where the NC response for wood samples was much lower and the ratio of NG response to NC response was two orders of magnitude higher. However, the NG response by the Modified CRREL method was similar to that observed in the bench test (correcting for extraction volumes and dilution) and suggests that conversion of N to nitrite for NG is substantially complete or at least similar in completeness for both methods.

Figure 3-4



Wood Sample Analysis

The results of wood sample extract analyses by the Modified CRREL method are tabulated in Table 3-7. This table also shows STL results for MCAWW 353.2 for NC and Method 8330 for NG and the corrected total for STL NC and NG results. DROPEX^{Plus} / EXPRAY™ and GC/TID results for the sample extracts are also shown for comparison. Concentrations of both NG and NC were detected in many of the samples, so calculation of CRREL results were performed as NC and as NG and both results are included in the Table 3-7. Since NC was detected in more samples than NG and typically at substantially higher concentrations, the CRREL results calculated as NC were used in the comparison to STL reference method results. Results for NG QC sample analyses for NG spike laboratory control samples (LCS); NG matrix spike (MS) and matrix spike duplicate (MSD) samples were calculated as NG.

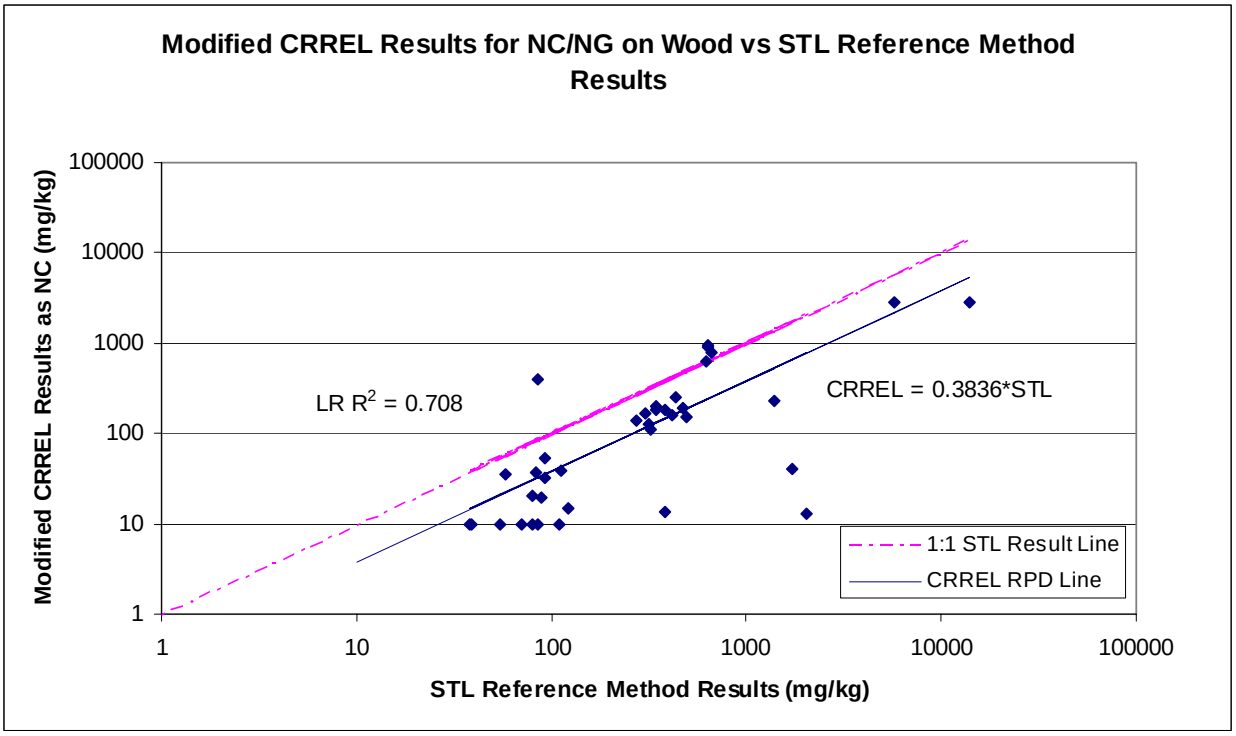
The detection limit using the Modified CRREL method for the wood samples was 10 mg/kg for NC and 5 mg/kg for NG in undiluted samples. There were 33 wood samples analyzed, four (4) of them were analyzed in duplicate. NC was detected in all 33 (including duplicates) by the STL MCAWW 353.2 method at concentrations ranging from 38 mg/kg to 14,000 mg/kg. NG was detected in twelve (12) of these samples by the STL Method 8330 method at concentrations ranging from 3.7 mg/kg to 240 mg/kg. The Modified CRREL method detected NC/NG in 27 of the samples at NC concentrations ranging from 13 mg/kg to 2,820 mg/kg.

There were zero false positive results for the Modified CRREL method and 7 out of 37 analyses or 18.9 percent that gave false negative results. The false negatives were for the samples that were non-detect by the CRREL method, and STL reported values in the range of 38 mg/kg to 109 mg/kg. The STL MCAWW 353.2 analysis results were qualified because of contamination in the method blanks that ranged from 5.8 mg/kg to 9.4 mg/kg, and after applying the wood matrix correction, resulted in blank values equal to 12-19 mg/kg on a sample basis. The positive STL blank values indicate the possibility of false positives in the STL data and high bias in results, especially at the lower concentrations. This should be taken into consideration before placing too much significance on the accuracy of the STL wood sample results, especially the lower concentration results. The bench test results also showed that the STL MCAWW 353.2

results were consistently biased high, especially at lower NC concentrations and NC was detected in unspiked clean background samples.

The average CRREL/STL RPD for the results data set was 89.1 percent and the standard deviation of the RPD data set was 69.9 percent indicating that the results have considerable scatter in agreement and the CRREL results are clearly biased low compared to the STL results. Figure 3-5 shows a correlation plot of quantitative results for wood sample analyses for the Modified CRREL method versus the total STL reference method results. The upper line shows the ideal 1:1 correlation line and the lower line shows the values for the average CRREL RPD with respect to the STL results. The average CRREL RPD line is at 38.4 percent of the STL reference method values, and this is equal to the average ratio for the Modified CRREL result obtained relative to the STL result.

Figure 3-5



There are no clear explanations for the high RPD in results between the methods. The first consideration, however, is the potential high bias in the STL MCAWW 353.2 results, especially at lower concentrations, that was indicated by positive results in method blanks and demonstrated in the bench test. A high bias may be due to matrix interference with the method and this effect could be systemic to the wood results. In the bench test, uncorrected MCAWW 353.2 results for two analyses of unspiked clean background wood were both 14.2 mg/kg NC. With the matrix correction applied these results would both be 28.2 mg/kg. A second consideration is the matrix correction applied to the STL MCAWW 353.2 results. The results were corrected using bench test data that increased the reported values by a factor of 1.98 or a 98% increase. This factor may have changed since the bench test because of method modifications, difference in wood matrix, etc., but even if the results were not corrected, there would still be a detectable negative bias. Finally, the high degree of scatter in results agreement may be due to the small aliquot size used in the wood analysis by the STL MCAWW 353.2 reference method. Typically 10 grams are used, but for the wood samples 2 grams were used because of the sample bulk, and this increases the probability of sample non-homogeneity

effects. The smaller a sample aliquot is that is used in an analysis the more likely it is to obtain aliquots that differ in composition. For the CRREL method, 20 grams were used, the same size aliquot that was used for soil and concrete matrices, but larger solvent volume and sample bottles were used for extraction. The results for duplicate sample pair analyses gave results within 40 percent RPD for three out of four of the pairs for the STL reference method and 4 out of 4 for the Modified CRREL method; however, and this does not indicate a significant problem with precision for either method.

There is difficulty in validating the Modified CRREL method by comparing sample analysis results to those from the STL MCAWW 353.2, since there is no validation data that asserts the validity of either of the methods. These analyses are showing that there is some degree of bias with either one or both the methods. Analysis of NC is affected by a lack of standard material, potential for incomplete extraction from the matrix and analysis chemistry that seems to be impacted by adverse sample matrices. The task may be manageable by validating NC extraction using spiked matrices as was done in the bench tests but using the Modified CRREL rather than the CRREL RDX method that was used. In the bench test the reference method demonstrated a positive bias below about 50 mg/kg, so concentrations at or below this level will not be accurately quantified by this method unless modifications are made. Using spiked matrices the method results can be compared to prepared concentrations for absolute bias assessment. Matrix samples along with matrix spike samples can be used to assess method performance on actual samples and again have prepared spike concentrations for comparison to assess performance. Also, it would be useful to compare results for analysis of sample extract splits by both the field and reference methods to assess method differences when analyzing the same extract. This would eliminate sample non-homogeneity issues. Finally, prepared NC spike/standard solutions from both labs should be analyzed by both labs to incorporate potential differences in standard concentrations into the data assessment.

Table 3-7 Modified CRREL Results for Wood Samples

	STL Reference Method Results (mg/kg)				Shaw Modified CRREL NG+NC		NG GC/TID	Drop-Ex	Expray
Sample Identification	Method 8330 NG	Method 353.2 NC	Corr. Method 353.2 NC	Corr. Total NG+NC	Analyzed conc as NG	Analyzed conc as NC	Conc mg/Kg	Extract (10 uls)	Extract (10 uls)
6657-02N-WD-001	3.7J	190JB	377	381	5	13	ND<5.0	-	-
6657-02N-WD-002	18	851Q,JB	1690	1710	25	40	3.22 J	-	-
6657-02I-WD-003	ND<0.5	39.9JB	79	79	ND<5	ND<10	ND<5.0	-	-
6657-02I-WD-003A	ND<5	43.2JB	86	86	ND<5	ND<10	ND<5.0	-	-
6657-02I-WD-004	ND<0.5	1020Q,JB	2020	2020	4	13	ND<5.0	-	-
5024-000-WD-005	ND<5	221JB	438	438	172	250	7.67	+	-
5024-000-WD-006	ND<5	174JB	345	345	122	184	ND<5.0	+	-
5024-000-WD-007	ND<5	697Q,JB	1380	1380	158	231	ND<5.0	+	-
5024-000-WD-008	ND<5	40.5JB	80	80	10	20	ND<5.0	-	-
5024-000-WD-009	ND<0.5	44.6JB	88	88	9	19	ND<5.0	-	-
5024-000-WD-010	ND<5	332JB	659	659	579	806	ND<5.0	++	++
5024-000-WD-011	ND<2.5	138JB	274	274	95	137	ND<5.0	+	+
6709-17-WD-012	99	143JB	284	383	101	180	31.6	+-	-
6709-17-WD-013	88	115JB	228	316	62	129	19.2	+	-
6709-17-WD-014	230	198JB	393	623	442	627	98.3	+	+
6709-17-WD-015	240	198JB	393	633	661	914	104	+	++
6709-17-WD-016	180	156JB	310	490	79	152	47.3	+-	-
6709-17-WD-017	130	172JB	341	471	106	187	44.5	+-	-
6709-17-WD-018	84	122JB	242	326	49	111	22.9	+	-
6709-17-WD-019	120	149JB	296	416	84	157	44.5	+	-
6709-17-WD-020	110	96.2JB	191	301	90	165	25.4	+	-
6709-17-WD-020A	120	113JB	224	344	120	204	25.9	+	-
6709-17-WD-021	62	286JB	567	629	682	965	58.5	++	++
1890-01-WD-022	ND<0.5	35.3JB	70	70	ND<5	ND<10	ND<5.0	+-	-
1890-01-WD-023	ND<0.5	19.1JB	38	38	ND<5	ND<10	ND<5.0	-	-
1890-01-WD-024	ND<0.5	27.6JB	55	55	ND<5	ND<10	ND<5.0	-	-
1890-01-WD-025	ND<0.5	61.8JB	123	123	6	15	ND<5.0	+-	-
1890-01-WD-026	ND<0.5	19.8JB	39	39	ND<5	ND<10	ND<5.0	-	-
1890-01-WD-027	ND<5	46.3JB	92	92	20	33	ND<50	+	-
1890-01-WD-028	ND<5	29.1JB	58	58	21	35	ND<5.0	-	-
1890-01-WD-028A	ND<5	42.4JB	84	84	23	37	ND<5.0	-	-
1890-01-WD-029	ND<5	56.5JB	112	112	24	39	ND<5.0	-	-
1890-01-WD-030	ND<5	46.6JB	92	92	35	53	ND<5.0	+-	-
9590-000-WD-031	ND<0.5	42.9JB	85	85	285	397	ND<5.0	+	-
9590-000-WD-032	ND<10	54.8JB	109	109	ND<5	ND<10	ND<50	-	-
5024-000-WD-033	ND<0.5	2880Q,JB	5710	5710	1830	2870	ND<20	+++	+++

Q= Elevated reporting Limit
J = Estimated result. Result is less than reporting limits.
JS = Estimated result. Surrogate recovery is outside stated control limits and reanalysis was outside hold time.
JB = Estimated result. Method blank contains contamination.
PG = The percent difference between the original and confirmation analysis is greater than 40%.
ND = Not detected at the specified method detrection limit
NA = Not analyzed or not applicable
+ = Detected
- = Not detected
+- = Possible detection; slight coloration, but difference from blank color was inconclusive

3.2.6 Soil

Calibration

An initial set of soil samples collected in the first week of the field demonstration were analyzed on-site by the CRREL RDX method. Subsequently, a second set of soil samples were submitted near the end of the on-site testing and these samples were returned to the Shaw Lab in Knoxville, TN for analysis by the CRREL RDX method. In addition, after the development of the Shaw Modified CRREL method at the Shaw Lab, sample extracts with sufficient volume for re-analysis were analyzed by this method to assess performance on the soil matrix. Separate calibration curves were prepared for the Shaw Modified CRREL and the CRREL RDX methods using NC and NG spiked onto background soil material prepared for the bench test.

Calibration curves for NC and NG in soil extracts using the CRREL RDX procedure were obtained during the field tests and used for the analysis of both the first set and the second set (at the Shaw Lab) of soil sample extracts. Table 3-8 shows a comparison of the standard concentrations for NC and method responses obtained for both CRREL methods. The data show that the response for NC by the modified method is on the order of 50-100 times greater than the CRREL RDX method and suggests that the CRREL RDX procedure on soil extracts converts less than about ten percent of the NC nitrogen (N) to nitrite for analysis. The results are consistent with those obtained for the wood samples, but the NC response by the CRREL RDX method was not as affected by the soil matrix and allowed calibration and sample analysis on undiluted extracts, although at elevated detection limits due to the lower response.

Table 3-8. Comparison of CRREL Method Calibration Results for Soil

CRREL RDX Method Field Demonstration Soil Calibration Sample Analyses		Shaw Modified CRREL NC/NG Method Field Demonstration Soil Calibration Sample Analyses	
mg/kg NC	Absorbance	mg/kg NC	Absorbance
0	0.025	0	0.000
25	0.036	1.5	0.067
50	0.071	5	0.239
100	0.308	10	0.411
200	0.447	15	0.742
500	0.529	NA	NA

Figures 3-6a and 3-6b show the NC and NG calibration curves for both CRREL methods. The plots show that NG response was not significantly different for the methods and suggests the N conversion from NG to nitrite is substantially complete for both methods with soil samples. The calibration response for NG was 71.4 times that of NC by the CRREL RDX method and 1.22 by the Modified CRREL method. The NC/NG response ratio for the Modified CRREL method is similar to that obtained for wood samples and is close to the expected theoretical ratio (1.31) based on the ratio of N content of NG to the N content of NC as discussed for the wood matrix samples. The increase in NC response provided by the Modified CRREL procedure is a big advantage for this method not only because of the increase in NC sensitivity, but also because of the similarity in responses that result for NC and NG. As a total method for NC and NG with similar responses for both analytes, calibration can be performed with only one of these and results for samples containing both NC and NG should be within acceptable accuracy for the total concentration. With a response ratio of NG to NC at the theoretical ratio of 1.31 the

relative percent difference (RPD) for a result calculated as NG compared to a result calculated as NC would be 27 percent. This is still within the acceptable performance range for accuracy of the CRREL screening method of 40 percent.

Figure 3-6a

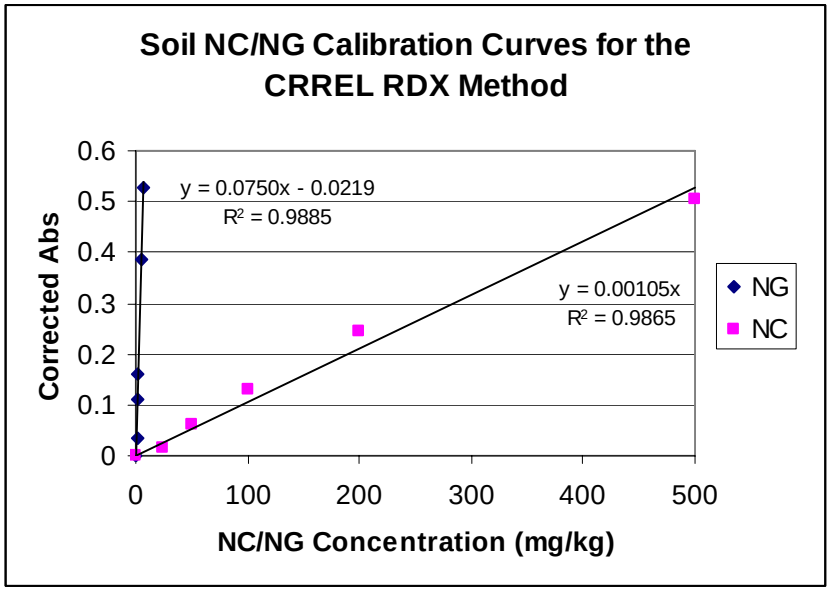
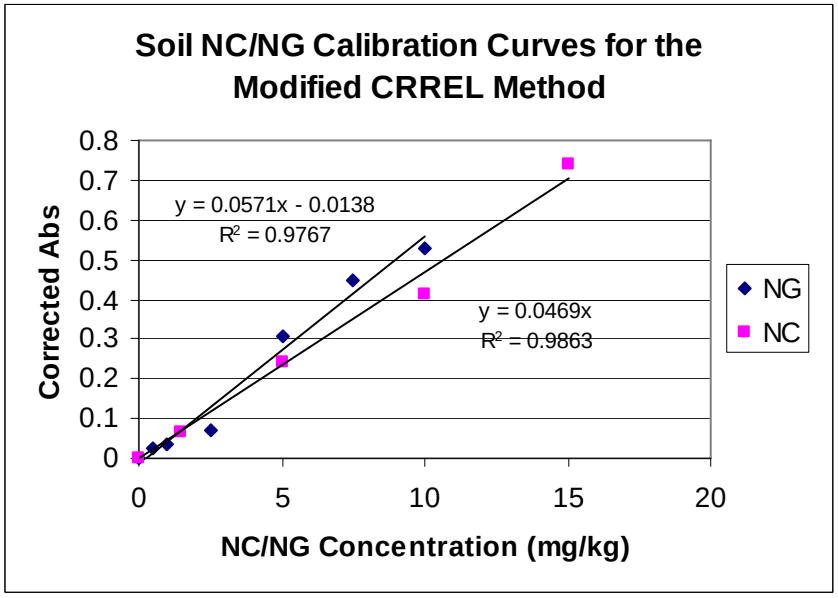


Figure 3-6b



Soil Sample Analysis

The results of soil sample extract analyses by the CRREL RDX method and the Modified CRREL method for NC/NG are tabulated in Table 3-9. This table also shows STL results for MCAWW 353.2 for NC and Method 8330 for NG and the corrected total for STL NC and NG results. DROPEX^{Plus} / EXPRAY™ and GC/TID results for the sample extracts are also shown for comparison. Concentrations of NG were detected in only a few of the samples and the levels were substantially below those for NC, so only results quantified as NC are shown in the Table 3-9. Results for NG QC sample analyses for NG spike laboratory control samples (LCS); NG matrix spike (MS) and matrix spike duplicate (MSD) samples were calculated as NG.

Two samples, 1885-02-SS-072 and 1885-02-SS-073, had pieces of propellant material physically removed during visual inspection at the time of sample preparation. Sample -072 had 0.023 grams removed from 695 grams of soil or 33.1 mg/kg. Sample -073 had 0.56 grams removed from 445 grams of soil or 1,260 mg/kg.

The detection limit using the CRREL RDX method for the soil samples was 25 mg/kg for NC and 1.0 mg/kg for NG in undiluted samples. The detection limit using the Modified CRREL method for the soil samples was 1.5 mg/kg for NC and 0.5 mg/kg for NG in undiluted samples. There were 33 soil samples analyzed, four (4) of them were analyzed in duplicate. There were only 27 of the samples that were analyzed by the Modified CRREL method due to limitations in the amount of sample extract available for re-analysis of six (6) of the samples. NC was detected in all 33 samples (including duplicates) by the STL MCAWW 353.2 method at concentrations ranging from 4 mg/kg to 10,300 mg/kg. NG was detected in ten (10) of these samples by the STL Method 8330 method at concentrations ranging from 0.18 mg/kg to 3.0 mg/kg. The CRREL RDX method detected NC/NG in 12 of the samples at NC concentrations ranging from 30.5 mg/kg to 7,500 mg/kg. The Modified CRREL method detected NC/NG in 20 out of 30 samples analyzed at NC concentrations ranging from 7 mg/kg to 8,610 mg/kg.

There was one (1) false positive result (2.7%) for the CRREL RDX method and 14 out of 37 analyses or 37.8 percent that were false negatives. For the Modified CRREL method there were zero false positive results and 10 out of 31 analyses or 32.3 percent that were false negatives. However, six (6) of the STL results for the false negatives were relatively low concentrations (4 mg/kg to 18 mg/kg) near the detection limit where there is greater variability and probability for false indication. Some of the STL MCAWW 353.2 analysis results were qualified because of contamination in the method blank. Two of the three STL method blanks contained detectable amounts of NC at values of 1.3 mg/kg and 2.9 mg/kg, and after applying the soil matrix correction, the blank values were equal to 2 mg/kg and 4 mg/kg on a sample basis. The positive STL blank values indicate the possibility of false positives in the STL data and high bias in results, especially at the lower concentrations. This should be taken into consideration before placing too much significance on the accuracy of the STL soil sample results, especially the lower concentration results. The bench test results also showed that the STL MCAWW 353.2 results were consistently biased high, especially at lower NC concentrations and NC was detected in unspiked clean background samples. Nevertheless, omitting the questionable six (6) STL detections would still leave 4 out of 31 analyses or 12.9 percent false negatives

The average CRREL/STL RPD for the CRREL RDX method data set was 82.7 percent and the standard deviation was 81.8 percent. For the Modified CRREL results data set the average CRREL/STL RPD was 82.7 percent and the standard deviation was 72.0 percent. This data is similar to what was obtained for wood samples and similarly indicates considerable scatter in results agreement and a low bias for the CRREL results compared to the STL results. The STL

comparison results for the two CRREL methods were similar and indicate agreement between the two CRREL methods. The average RPD between the results for the CRREL RDX method and the Modified CRREL method was 36.5 percent, which is within the 40 percent accuracy expectation for the CRREL RDX method. Figure 3-7 and Figure 3-8 show correlation plots of quantitative results for wood sample analyses for the CRREL methods versus the total STL reference method results. The upper line in both plots shows the ideal 1:1 correlation line and the lower line shows the values for the average CRREL RPD with respect to the STL results. It can be seen that the data for the CRREL RDX method are influenced by the higher detection limit. The average CRREL RPD line is at 41.5 percent of the STL reference method values for both CRREL methods and this value is equal to the average ratio for the CRREL result obtained by either method relative to the STL result. The biggest difference between the two CRREL methods is the correlation of results to the STL results. The CRREL RDX method has a linear regression (LR) correlation coefficient (R^2) value of 0.8979 while the Modified CRREL method has a correlation coefficient of 0.9548, which meets the method comparison performance criterion of greater than 0.95

Figure 3-7

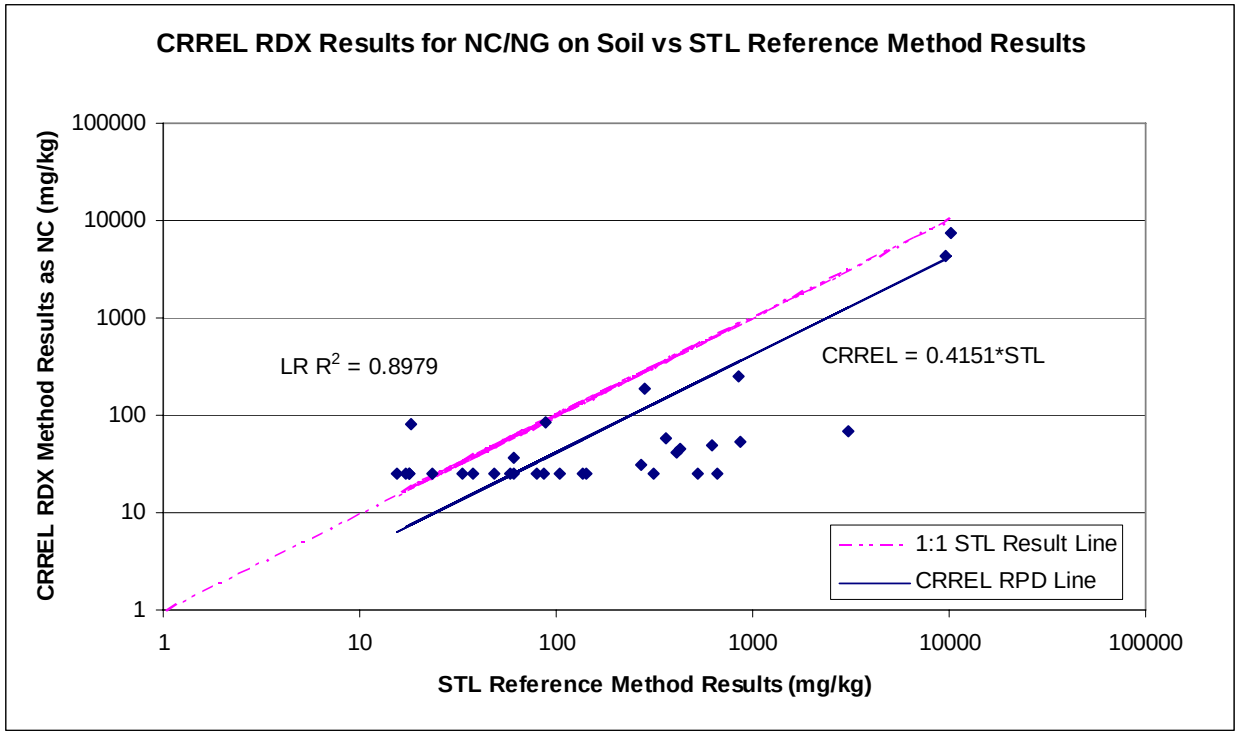
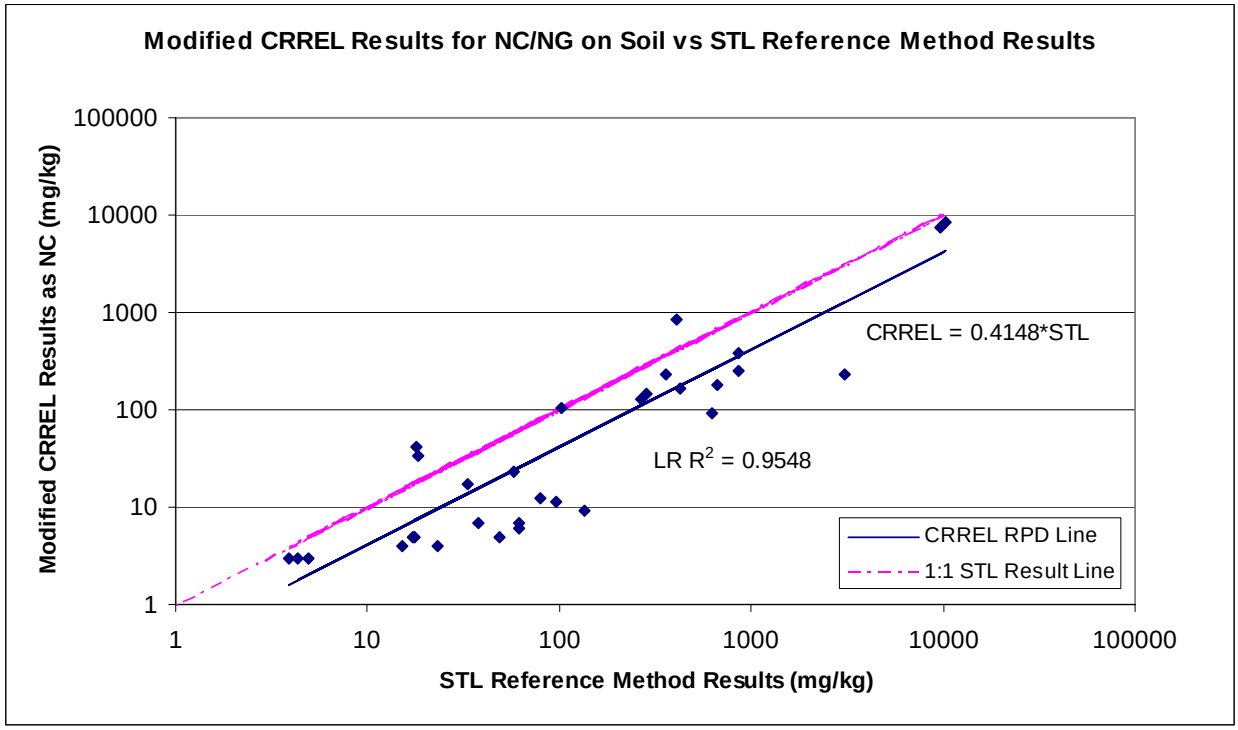


Figure 3-8



There are no clear explanations for the high RPD in results between the methods. The first consideration, however, is the potential high bias in the STL MCAWW 353.2 results, especially at lower concentrations, that was indicated by positive results in method blanks and also demonstrated by a positive result for unspiked clean background soil in the bench test (test verification sample). A high bias may be due to matrix interference with the method and this effect could be systemic to the soil results. A second consideration is the matrix correction applied to the STL MCAWW 353.2 results. The STL results for MCAWW 353.2 were corrected for the soil matrix using bench test data that increased the reported values by a factor of 1.55 or a 55% increase. This factor may have changed since the bench test because of method modifications, difference in soil matrix, etc., but even if the results were not corrected, there would still be a significant negative bias. Finally, the high degree of scatter in results agreement is believed to be due to sample non-homogeneity and this is highly probable because of pieces of NC/NG propellant material, such as those picked out of the two samples described above, that may be grabbed in a sample aliquot The results for duplicate sample pair analyses gave results within 40 percent RPD for only one out of four of the pairs for the STL reference method and 2 out of 3 (one pair was a pair of non-detect results) for the Modified CRREL method, which supports the explanation.

Table 3-9 CRREL Results for Soil Samples

Sample Identification	STL Reference Method Results (mg/kg)				CRREL NG+NC	Modified CRREL	GC/TID NG	Drop-Ex	Expray
	Method 8330 NG	Method 353.2 NC	Corr. Method 353.2 NC	Corr. Total NG+NC	Conc as NC mg/kg	Conc as NC mg/kg	Conc mg/Kg	Extract (10 uls)	Extract (10 uls)
1885-02-SS-067	ND<0.5	203Q	314	314	ND<25	ND<57	ND<2.0	+	+
1885-02-SS-068	0.55	551Q	852	853	256	382	ND<2.0	++	++
1885-02-SS-069	0.36J,JS	400Q	619	619	ND<50	91	ND<2.0	++	+
1885-02-SS-070	ND<0.5	57.6	89	89	82.9	NS	ND<2.0	++	+
1885-02-SS-071	ND<0.5	11.2	17	17	ND<25	ND<5	ND<2.0	-	-
1885-02-SS-072	2.1JS	6200Q	9590	9590	4290	7570	22.0	+++	++
1885-02-SS-072A*	1.4PG,JS	6640Q	10300	10300	7500	8610	44.5	++++	+++
1885-02-SS-073*	ND<0.5	11.8	18	18	80.0	34	ND<2.0	+	-
1885-03-SS-074	ND<0.5	2.5	4	4	ND<25	ND<3	ND<2.0	-	-
1885-03-SS-075	ND<0.5	39.6	61	61	37.1	ND<7	ND<2.0	-	-
1885-03-SS-076	ND<0.5	51.3	79	79	ND<25	12	ND<2.0	+-	-
1885-03-SS-077	ND<0.5	15.0	23	23	ND<25	ND<4	ND<2.0	-	-
1885-03-SS-078	ND<0.5	31.4	49	49	ND<25	ND<5	ND<2.0	-	-
1890-01B-SS-079	ND<0.5	3.2	5	5	ND<25	ND<3	ND<2.0	-	-
1890-01B-SS-080	0.55JS	182Q	282	282	185	147	3.0	+	+
1890-01B-SS-081	ND<0.5	11.6	18	18	ND<25	42	ND<2.0	+	+-
1890-01B-SS-081A	ND<0.5	39.5	61	61	ND<25	ND<6	ND<2.0	-	-
1890-01B-SS-081(B)	NA	NA	NA	NA	NA	ND<5	NA	NA	NA
1890-01B-SS-081(C)	NA	NA	NA	NA	NA	ND<5	NA	NA	NA
1885-02-SS-082	1.0	1970Q, JB	3050	3050	68.6	235	ND<2.0	+	++
1885-02-SS-083	3.0JS	275Q,JB	425	428	44.8	163	ND<2.0	+	++
1885-02-SS-083A	ND<0.5JS	431Q,JB	667	667	ND<25	183	ND<2.0	+	+
1885-02-SS-084	ND<0.5	234Q,JB	362	362	57.1	233	ND<2.0	+	+
1885-02-SS-085	0.19J	174Q,JB	269	269	30.5	127	ND<2.0	+	+
1885-02-SS-086	ND<0.5	21.4JB	33	33	ND<25	17	ND<2.0	-+	-
1885-02-SS-087	0.82	558Q,JB	863	864	53.3	251	ND<2.0	+	+
1885-02-SS-088	0.39J	11.2JB	17	18	ND<25	ND<5	ND<2.0	-	-
1885-02-SS-089	ND<0.5	24.4JB	38	38	ND<25	7	ND<2.0	-	-
1885-02-SS-090	ND<0.5	2.8J, JB	4	4	ND<25	ND<3	ND<2.0	-	-
1885-02-SS-091	ND<0.5	266Q,JB	412	412	41.9	838	ND<2.0	+	+
1885-02-SS-092	ND<0.5	37.4JB	58	58	ND<25	23	ND<2.0	+	-+
1885-02-SS-093	0.18J	340Q,JB	526	526	ND<25	ND<45	ND<2.0	-	-
1885-02-SS-093A	ND<0.5	92.2Q,JB	143	143	ND<25	ND<15	ND<2.0	-	-
1885-02-SS-094	ND<0.5	9.9JB	15	15	ND<25	ND<4	ND<2.0	-	-
1885-02-SS-095	ND<0.5	66.8JB	103	103	ND<25	104	ND<2.0	-+	+
1885-02-SS-096	ND<0.5	2.3J,JB	4	4	ND<25	NS	ND<2.0	-	-
1885-02-SS-097	ND<0.5	87.9Q,JB	136	136	ND<25	9	ND<2.0	+-	-
1885-02-SS-098	ND<0.5	55.7JB	86	86	ND<25	NS	ND<2.0	++	+
1885-02-SS-099	ND<0.5	62.5JB	97	97	NA	11	ND<2.0	+	+-

* = Propellant pieces removed from samples 72A and 73

(B) (C) = triplicate analysis

Q= Elevated reporting Limit

J = Estimated result. Result is less than reporting limits.

JS = Estimated result. Surrogate recovery is outside stated control limits and reanalysis was outside hold time.

JB = Estimated result. Method blank contains contamination.

PG = The percent difference between the original and confirmation analysis is greater than 40%.

ND = Not detected at the specified method detrection limit

NA = Not analyzed or not applicable

+ = Detected

- = Not detected

+- = Possible detection; slight coloration, but difference from blank color was inconclusive

3.2.7 Concrete

Calibration and Matrix Testing

Extracts of the top one to one and one-half inch of concrete core samples and two concrete core bottom samples (one to one and one-half inch of concrete core bottom) were analyzed on-site by the CRREL RDX method. In addition, after the development of the Shaw Modified CRREL method, concrete NC standard samples were analyzed at the Shaw Lab in Knoxville by the modified method to assess performance on the concrete matrix. Only two concrete core samples had positive results for NC by the CRREL RDX method and these samples were re-analyzed by the Modified CRREL method as well at the Shaw Lab. Concrete standard samples prepared using suspended NC fibers in water were also analyzed at the Shaw Lab by the CRREL RDX and Modified CRREL methods to evaluate the response compared to standards prepared using spike solutions of NC dissolved in acetone.

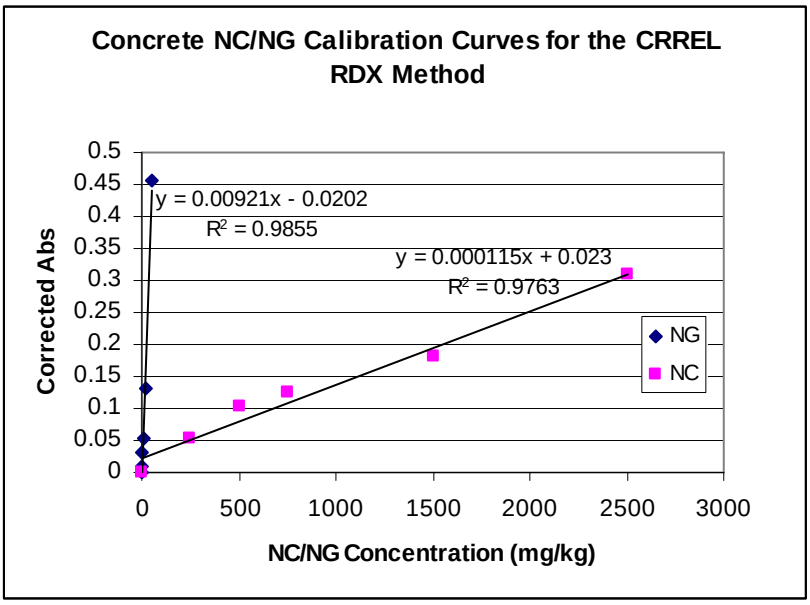
Separate calibration curves were prepared for the Shaw Modified CRREL and the CRREL RDX methods using NC spiked onto background concrete material prepared for the bench test. The calibration for NG on concrete was only performed on-site during the field demonstration using the CRREL RDX method for analysis.

Extracts of expanded joint material (EJM), a somewhat hard, dry, rubbery material that was used between concrete slabs to allow expansion of the slabs were also analyzed at the Shaw Lab. Since there was no background material to make matrix specific standards for calibration, background concrete matrix extracts were spiked with NC after matrix extraction and separation to prepare a calibration curve. NC was used for calibration because it was found at substantially higher concentrations than NG in concrete samples where NG was detected.

CRREL RDX Method Calibration in the Field

During the bench test NG calibration with the CRREL RDX method could not be performed and this was attributed to decomposition of NG by hydrolysis due to the alkalinity of the concrete matrix. In the field demonstration, concrete standards were extracted immediately after being spiked with NG or NC in acetone to minimize time on the matrix and maximize analyte recovery. This was different than what was done in the bench test. In the bench test the NC spike solutions were composed of fine fibrous NC suspended in aqueous solution. After matrix material was spiked, overnight drying of the material was required to remove water added from the spike solution before it could be extracted with acetone. For NG in the bench test, spiked materials were also allowed to dry overnight for more complete incorporation of NG into the matrix as a better representation of actual sample material containing NG. This was done before analyte recovery problems were discovered and suspicions of decomposition on the matrix were formulated. As a result of the procedure changes for the field demonstration, a standard calibration was achieved for both NG and NC with the CRREL RDX method. The curves obtained are shown in Figure 3-9. The NC/NG response ratio (80.1) was similar to what was obtained with the CRREL RDX method on the soil matrix (71.4); however, the absolute responses for both analytes were a factor of eight to nine times lower for the concrete matrix. This indicated that either decomposition was still affecting analyte recovery or the matrix was interfering with either the extraction efficiency or the method chemistry.

Figure 3-9



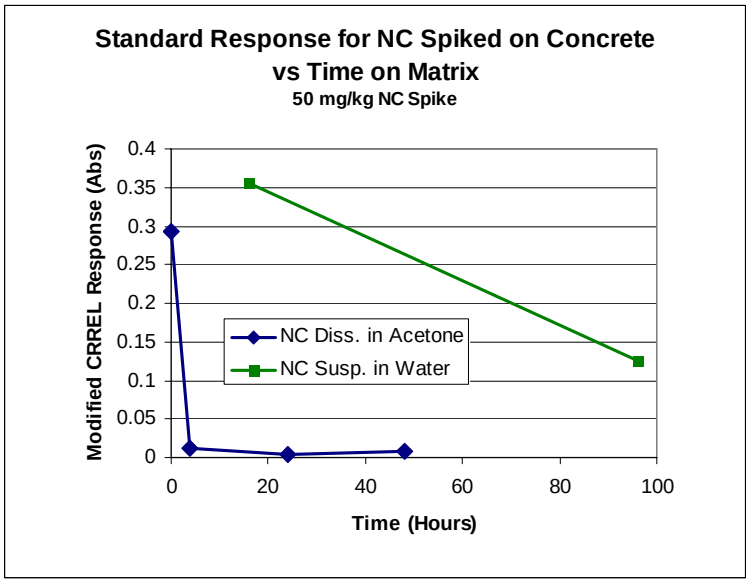
Compared to the results obtained in the bench test, the response for NG was greatly improved, but the response for NC was only marginally better. It was noted however in the bench test that NC was not as affected by the concrete matrix as was NG and this suggested NC was more stable with respect to decomposition by the matrix. However, what was not considered in the bench test was the difference in spiking procedure. It is now reasoned that the use of analyte dissolved in acetone for matrix spiking provides more intimate contact with the matrix (molecular level) than does the use of fibrous particulate and that this may be the reason NC was not as affected by the matrix as NG in the bench test. NC was also used at much higher concentrations, so there was a higher level of loading and greater chance of recovering some NC to obtain a response during analysis. Nevertheless, the use of NC dissolved in acetone for the field demonstration may have altered the extraction efficiency or increased decomposition effects.

NC Stability on Concrete Tests

When the Modified CRREL method was used at the Shaw Lab to analyze prepared NC concrete standards the response for the standards was lower than that obtained for wood and soil, which must be due to matrix interference. To investigate the matrix interference, background concrete material was extracted with acetone and the extract was removed from the matrix and spiked with NC. This provided a matrix extract with a known amount of NC added for analysis by the Modified CRREL procedure. The response obtained for NC in this test was greater and was consistent with results obtained with wood and soil matrix standards. The results showed that the concrete matrix was not interfering with the method chemistry. By elimination it was concluded that the matrix was either interfering with NC extraction or was decomposing NC even on the time frame involved for standard preparation by the new procedure, which was on the order of minutes.

To investigate analyte stability on concrete matrix several tests were performed where NC was spiked onto background concrete matrix and the tests were extracted at different times after being spiked with NC. In addition, tests were performed with NC spiked onto concrete using a sheared fibrous NC suspension in aqueous solution as was done during the bench test. The data from these tests are summarized in Figure 3-10.

Figure 3-10

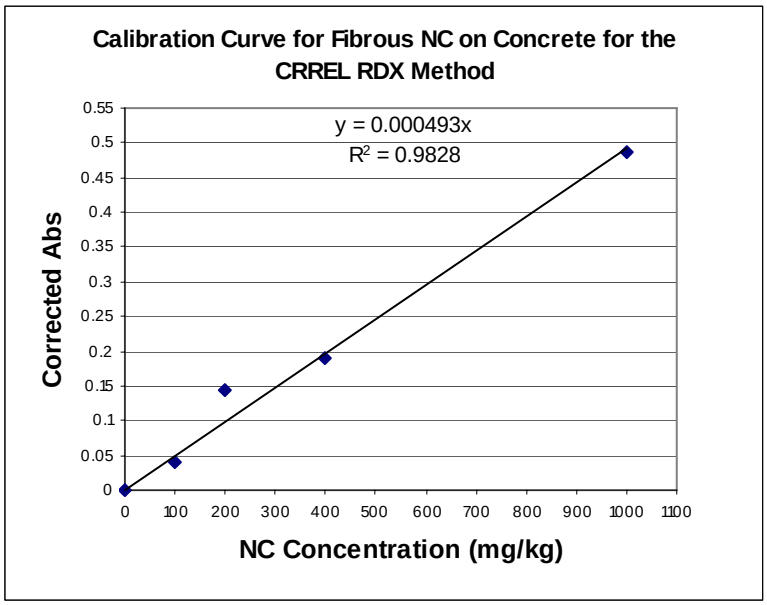


The results from these tests show two things. First, that recovery of NC from concrete decreases with time and this is most likely due to decomposition of NC by hydrolysis in the matrix. Secondly, the manner in which NC is deposited on the matrix affects its ability to be recovered, again, most likely due to decomposition. Particulate NC is more completely recovered from the matrix. The test using a 50 mg/kg NC spike dissolved in acetone was nearly below detection (less than 10% recovered) after only four (4) hours on the matrix, while about one third of the particulate NC was recovered after 96 hours. These results suggested that the ability to recover NC from the matrix would also be affected by the amount of NC deposited and the NC particle size, i.e., a higher NC loading and larger NC particle size would be more efficiently recovered, but these variables were not tested.

CRREL RDX Method Calibration with Particulate NC

The analyte stability tests on concrete demonstrated the difficulty in analyzing NC/NG in the concrete matrix. The ability to obtain a response for these analytes is dynamic, which more than likely depends on numerous factors as discussed above. Because of this, it is hard to imagine being able to prepare and analyze concrete matrix standards that can accurately reflect the nature of the analytes in actual samples. It may be best to use background concrete material to prepare extracts and then spike the extracts with NC/NG for analysis, but this may significantly bias results low, because it assumes no NC/NG loss to effects during the extraction process. For example, analytes that may be positioned in or on the sample matrix such that they are stable and extractable will be exposed to the matrix differently during the extraction process and may not be recovered efficiently. Because of these considerations, it was decided that the best alternative for NC analysis would be to assess how NC may be deposited in the matrix being analyzed and use standards prepared in a similar manner. For the field demonstration this may be to use standards prepared with the fibrous NC suspension and extract them as soon as possible. For NG there was no better alternative than to do what was done in the field and that was to spike matrix samples with the only NG spike source available and extract immediately. A standard curve for NC on concrete using a fibrous NC suspension by the CRREL RDX method was prepared at the Shaw Lab and the curve is shown in Figure 3-11. The curve obtained shows a response for NC that is about four (4) times greater than that obtained in the field using the NC in acetone spike solution for standard preparation.

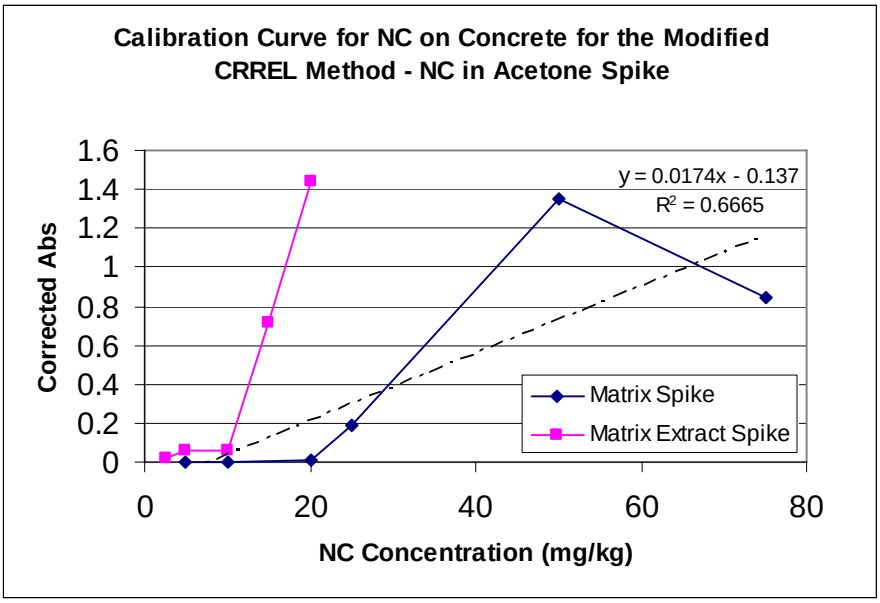
Figure 3-11



Modified CRREL Method Calibration

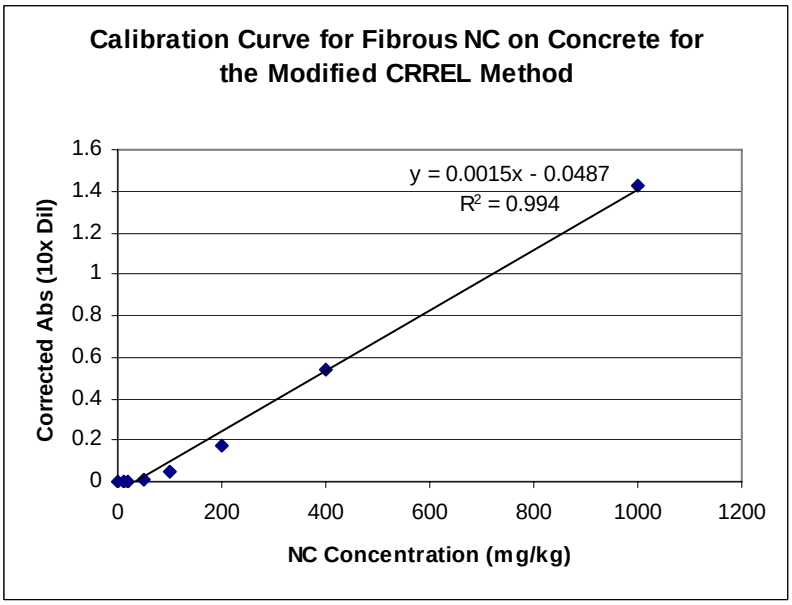
Calibration using the Modified CRREL method for NC on concrete was also performed to assess the performance of this method. A curve was prepared initially using concrete standards prepared with acetone spike solutions of NC and extracted immediately. Figure 3-12 shows the curve obtained. The figure shows a somewhat inconsistent trend for the response as a function of concentration and this was attributed to concrete matrix effects on the relatively low concentrations used with the Modified CRREL method. The standard concentrations for the Modified CRREL method ranged from 5 mg/kg to 75 mg/kg and those used for the CRREL RDX method (NC in acetone) ranged from 250 mg/kg to 2,500 mg/kg. The NC response by the Modified CRREL method for concrete standards was about one hundred times greater than the response with the CRREL RDX method. However, the response for the concrete standards by the Modified CRREL method was only about one third of that for either the wood or soil standards and indicates the relative degree of matrix interference. Also shown in this figure is a curve showing responses for standards prepared using NC spikes into background concrete matrix extract after extraction and separation from the matrix. These standards should not have had any matrix interference effects involving extraction problems or decomposition. The responses were much higher and the curve difference illustrates the degree of matrix interference obtained at the concentration levels for the Modified CRREL method. The curves also indicate loss of analyte at concentrations of 10 mg/kg and below to other effects not definitely identified, but may be related to loss during resin column treatment per the method. This is discussed in more detail below. Calibration curves for NG using the Modified CRREL method were not performed.

Figure 3-12



A calibration curve with concrete matrix standards prepared using fibrous NC spikes was also generated with the Modified CRREL method to assess the performance of the method with these standards. The standards were prepared at higher concentrations than what was anticipated for the method response range to minimize matrix effects. Prepared extracts were then diluted by a factor of ten for analysis by the method. The curve is shown in Figure 3-13. The response obtained was similar to that obtained for NC in acetone spiked standards when corrected for dilution. The curve was more consistent, but the standard concentrations were higher and that apparently had the desired effect of minimizing the impact of matrix effects.

Figure 3-13

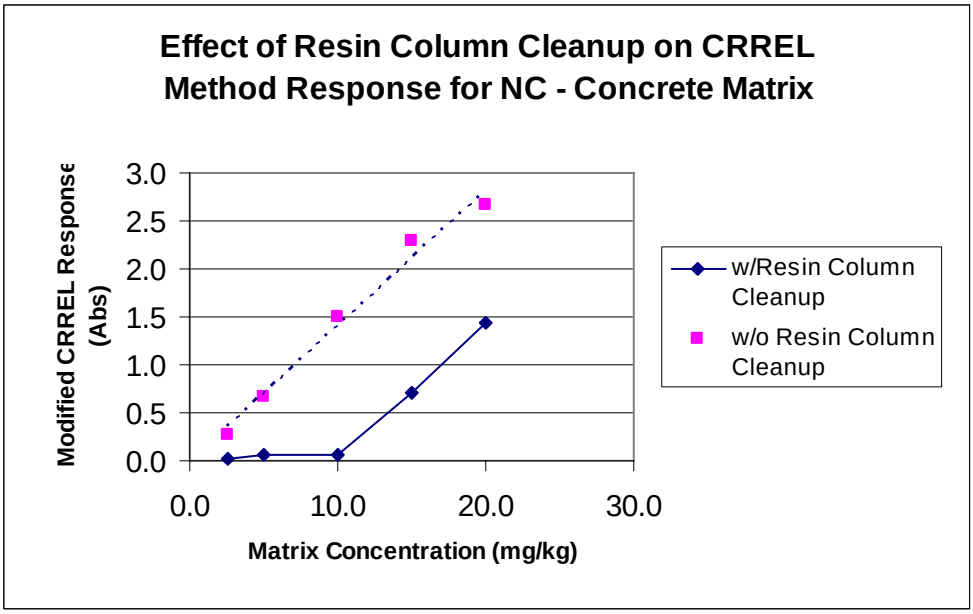


CRREL Method Resin Column Tests – Effect on NC Recovery

One other area of the CRREL methodology that was investigated during tests on concrete was the performance of the alumina ion exchange resin column used in the procedure. The recovery of analyte at relatively low concentrations from the column was investigated as part of the tests

performed to identify sources of interference with the concrete matrix. The resin column removes interferences including free nitrate and free nitrite ions prior to hydrolysis of the sample extract and subsequent color development. Tests were performed using background concrete extract spiked with NC to remove matrix contact effects but still have concrete extract as the analysis medium. Data from the bench test showed that the background concrete material contained less than 1 mg/kg of free nitrate or free nitrite, so column treatment to remove these ions was not necessary for this material. Extracts were spiked at five concentrations in the range of 2.5 to 20 mg/kg. The extracts were then analyzed by the Modified CRREL method using the method resin column cleanup and not using the resin column cleanup. Figure 3-14 shows the curves obtained. The data indicate that the resin column may hold onto about the first 10 mg/kg (concrete concentration basis) of NC, which is 10 mg/L extract concentration or 0.05 milligrams of NC (5 mL test). This loss was not noted in either the wood or soil sample testing and may be related to the concrete extract matrix or the batch of alumina columns that were used, since a new batch of columns was used for the concrete tests conducted at the Shaw Lab. This effect was not investigated further, since this level of interference was small with respect to the state of the methodology, i.e., a detection limit of 100 mg/kg. However, the effect illustrates the potential for this kind of interference and need for possible consideration during future testing and evaluation of the CRREL method.

Figure 3-14



Concrete Material Sample Analysis

Sample concentrations from CRREL RDX method analysis were quantified using calibration curves generated standards prepared with aqueous suspensions of NC spiked onto concrete. It was reasoned that contamination on concrete samples would be of a nature that is relatively stable because of the length of time involved for the history of the samples, and that this would be best represented by calibration with the NC particulate standards. Only two samples (-046 and -046A) had positive results for NC by the CRREL RDX method and they were also analyzed by the Modified CRREL method at the Shaw Lab. The results of concrete sample extract analyses are tabulated in Table 3-10. This table also shows STL results for MCAWW 353.2 for NC and Method 8330 for NG and the corrected total for STL NC and NG results. DROPEX^{Plus}/ EXPRAY™ and GC/TID results for the sample extracts are also shown for comparison.

Concentrations of NG were detected in only a few of the samples and the levels were substantially below those for NC, so only results quantified as NC are shown in the Table 3-10. Results for NG QC sample analyses for NG spike laboratory control samples (LCS); NG matrix spike (MS) and matrix spike duplicate (MSD) samples were calculated as NG.

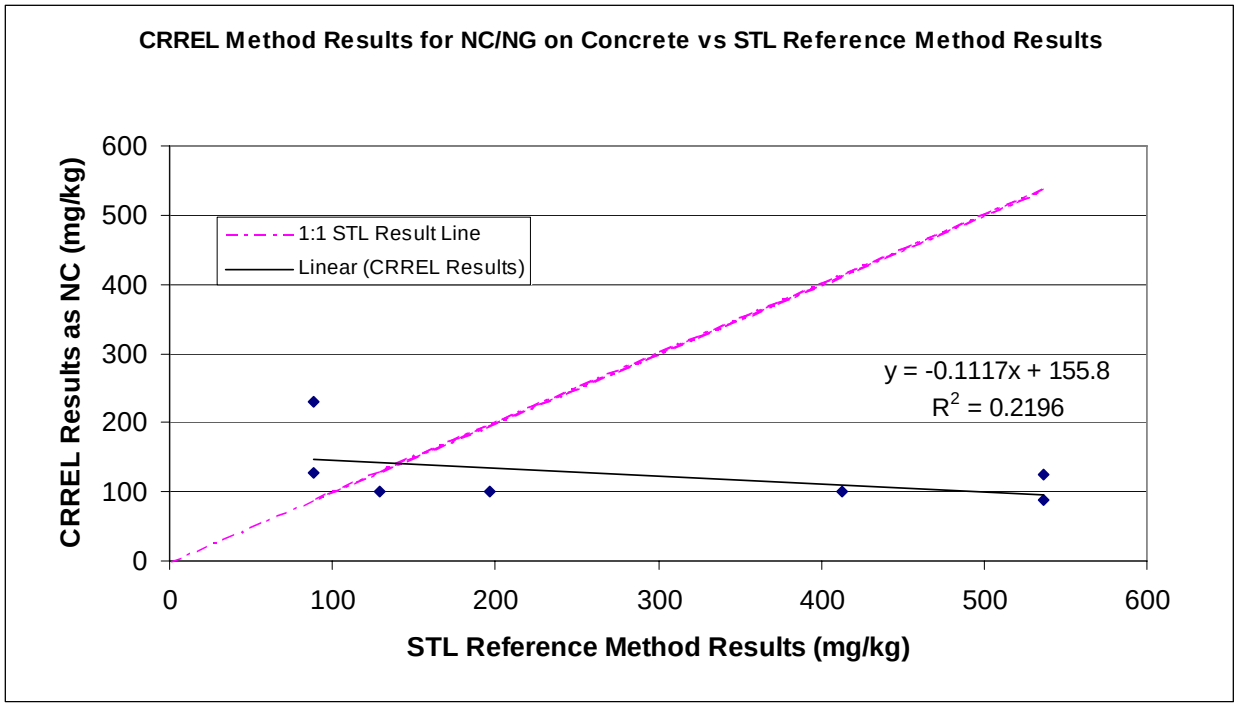
The detection limit using the CRREL RDX method for the concrete samples was 100 mg/kg for NC and 5.0 mg/kg for NG in undiluted samples. There were 37 concrete core top samples analyzed, four (4) of them were analyzed in duplicate and there were two (2) concrete core bottom samples (not submitted to STL). NC was detected in all 41 samples (including duplicates) by the STL MCAWW 353.2 method at concentrations ranging from 5 mg/kg to 536 mg/kg. NG was detected in three (3) of these samples by the STL Method 8330 method at concentrations ranging from 0.23 mg/kg to 1.1 mg/kg. The CRREL RDX method detected NC/NG in only two (2) of the samples, one sample (1890-01B-CM-046) and its duplicate (1890-01B-CM-046A), at NC concentrations of 124 mg/kg and 128 mg/kg (ND level was 100 mg/kg as NC). The Modified CRREL method detected NC/NG in the -046 sample as well at NC concentrations of 87 mg/kg and 230 mg/kg. Sample analyses for this sample by the modified method in duplicate are designated as samples 1890-01B-CM-046(B) and -046(C).

NC/NG was not detected in the two core bottom samples 1885-01-CM-035B and 1885-02-CM-100B neither analyzed by the CRREL RDX method nor was it detected in the corresponding core top samples. The DROPEX^{Plus} top surface wipe screens on both these cores indicated the presence of NC/NG. The bottom surface wipe screen on the -035 core also indicated the presence of NC/NG although it was not detected on the bottom of the -100 core.

There was one (1) false positive result (2.4%) for the CRREL RDX method at 128 mg/kg, but there was good agreement with the STL result (88 mg/kg) even though it was below the CRREL detection limit of 100 mg/kg, which classified this as a false positive. There were 5 out of 41 analyses or 12.2 percent that were false negatives. However, four (4) of the STL results for the false negatives were near the detection limit for the CRREL method where there is greater analytical variability and probability for false indication. . The bench test results also showed that the STL MCAWW 353.2 results were consistently biased high, especially at lower NC concentrations and NC was detected in unspiked clean background samples.

The average CRREL/STL RPD for the qualifying results data set was 42.2 percent and the standard deviation of the RPD data set was 40.0 percent. The data set was limited due to the number of non-detect results obtained for the CRREL method, but indicates a low or negative bias for the CRREL results compared to the STL results with the average CRREL result being 65.1 percent of the STL result. Figure 3-15 shows the correlation plot of quantitative results for concrete sample analyses for the CRREL methods versus the total STL reference method results. The axes are not logarithmic as they are for the wood and soil plots because the range of values was limited. The upper line in the plot shows the ideal 1:1 correlation line and the lower line shows the results of linear regression analysis of the qualifying CRREL data versus the STL results. The linear regression line shows there is little correlation between the CRREL results and the STL results and this is primarily attributed to the concrete matrix effect on the analytical process, which is likely method dependent. It is likely that non-homogeneity of NC/NG in the concrete sample also contributed to the non-agreement of results. Surface wipe screens indicated contamination of the core surface so sample results were likely affected by how many surface pieces or particles were included in the analysis aliquot grab. Finally, the data set was limited and only included two STL reference method analysis results that were significantly above the CRREL method detection limit of 100 mg/kg.

Figure 3-15



Expansion Joint Material Sample (EJM) Analysis

There were six concrete core samples that had expansion joint material (EJM) attached. EJM is a somewhat hard, dry, rubbery material approximately one-half to three-quarters of an inch in thickness that was placed in between concrete slabs to allow expansion. Because it is an organic matrix that may retain NC/NG contamination upon exposure and in a potential pathway for contamination to the underlying soil, there was interest in analyzing the material to assess levels of contamination. The EJM was scraped off the concrete core sample and was analyzed separately. The sample was labeled using an "EJM" identifier appended to the core sample designation to identify both the sample and its core source. The EJM was prepared for analysis in the same manner as the concrete, i.e., the material was crushed with a hammer to pieces of approximately one-quarter of an inch and collected in a Ziploc bag. The material was extracted for analysis by placing 5.0 grams of crushed material into a clean sample bottle, adding 50.0 milliliters of reagent acetone and agitating for an hour and a half. The extract was then removed from residual solids, filtered and analyzed by the Modified CRREL method for NC/NG. Sample responses were quantified by comparing to responses of standards prepared from NC spikes into background concrete material extract. A summary of the results obtained is shown in Table 3-11 along with the CRREL analyzed NC/NG concentration for the associated concrete core sample.

Table 3-10 CRREL Results for Concrete Material Samples

	STL Reference Method Results (mg/kg)				CRREL NG+NC	NG GC/TID	Drop-Ex	Expray
Sample Identification	Method 8330 NG	Method 353.2 NC	Corr. Method 353.2 NC	Corr. Total NG+NC	Analyzed conc as NC	Conc mg/Kg	Extract (10 uls)	Extract (10 uls)
9590-000-CM-034	ND<0.5	201Q	413	413	ND<100	ND<2.0	-	-
9590-000-CM-034A	ND<0.5	63.0	129	129	ND<100	ND<2.0	-	-
1885-01-CM-035	ND<0.5	17.1	35	35	ND<100	ND<2.0	+-	-
1885-01-CM-035B	NA	NA	NA	NA	ND<100	ND<2.0	+-	-
1885-01-CM-036	ND<0.5	20.3	42	42	ND<100	ND<2.0	-	-
1885-01-CM-037	ND<0.5	17.9	37	37	ND<100	ND<2.0	-	-
1890-01B-CM-038	ND<0.5	5.7	12	12	ND<100	ND<2.0	-	-
1890-01B-CM-039	ND<0.5	30.1	62	62	ND<100	ND<2.0	-	-
1890-01B-CM-040	ND<0.5	17.8	37	37	ND<100	ND<2.0	-	-
1890-01B-CM-041	ND<0.5	9.9	20	20	ND<100	ND<2.0	-	-
1890-01B-CM-042	ND<0.5	95.9Q	197	197	ND<100	ND<2.0	-	-
1890-01B-CM-043	ND<0.5	71.9Q	148	148	ND<100	ND<2.0	-	-
1890-01B-CM-043A	ND<0.5	36.8	76	76	ND<100	ND<2.0	-	-
1890-01B-CM-044	ND<0.5	10.2	21	21	ND<100	ND<2.0	-	-
1890-01B-CM-045	0.23J	87.8Q	180	180	ND<100	ND<2.0	-	-
1890-01B-CM-046	1.1	261Q	536	537	124	2.52	+	-
1890-01B-CM-046A	0.46J	42.7	88	88	128	1.44	+	-
1890-01B-CM-046(B)	NA	NA	NA	NA	87 [1]	NA	NA	NA
1890-01B-CM-046(C)	NA	NA	NA	NA	230 [1]	NA	NA	NA
1885-03S-CM-047	ND<0.5	3.1JB	6	6	ND<100	ND<2.0	-	-
1885-03S-CM-048	ND<0.5	3.0JM	6	6	ND<100	ND<2.0	-	-
1885-03S-CM-049	ND<0.5	6.8JM	14	14	ND<100	ND<2.0	-	-
1885-03S-CM-050	ND<0.5	3.4JM	7	7	ND<100	ND<2.0	-	-
1885-03-CM-051	ND<0.5	3.2JM	7	7	ND<100	ND<2.0	-	-
1885-03-CM-052	ND<0.5	5.3JM	11	11	ND<100	ND<2.0	-	-
1885-03-CM-053	ND<0.5	8.8JM	18	18	ND<100	ND<2.0	-	-
1885-03-CM-054	ND<0.5	5.0JM	10	10	ND<100	ND<2.0	-	-
1885-03-CM-055	ND<0.5	4.0JM	8	8	ND<100	ND<2.0	-	-
1885-03-CM-056	ND<0.5	9.8JM	20	20	ND<100	ND<2.0	-	-
1885-02-CM-057	ND<0.5	36.1JM	74	74	ND<100	ND<2.0	-	-
1885-02-CM-058	ND<0.5	3.1JM	6	6	ND<100	ND<2.0	-	-
1885-02-CM-059	ND<0.5	6.1JM	13	13	ND<100	ND<2.0	-	-
1885-02-CM-060	ND<0.5	8.7JM	18	18	ND<100	ND<2.0	-	-
1885-02-CM-061	ND<0.5	9.8JM	20	20	ND<100	ND<2.0	-	-
1885-02-CM-062	ND<0.5	7.3JM	15	15	ND<100	ND<2.0	-	-
1885-02-CM-063	ND<0.5	11.5JM	24	24	ND<100	ND<2.0	-	-
1885-02-CM-064	ND<0.5	4.2JM	9	9	ND<100	ND<2.0	-	-
1885-02-CM-065	ND<0.5	6.9JM	14	14	ND<100	ND<2.0	-	-
1885-02-CM-066	ND<0.5	7.6JM	16	16	ND<100	ND<2.0	-	-
1885-02-CM-100	ND<0.5	3.5JB,JM	7	7	ND<100	ND<2.0	-	-
1885-02-CM-100A	ND<0.5	4.4JB,JM	9	9	ND<100	ND<2.0	-	-
1885-02-CM-100B	NA	NA	NA	NA	ND<100	ND<2.0	-	-
1885-02-CM-101	ND<0.5	2.2JB,JM	5	5	ND<100	ND<2.0	-	-
1885-02-CM-102	ND<0.5	3.4JM,JB	7	7	81	ND<2.0	-	-
1885-02-CM-103	ND<0.5	3.5JM,JB	7	7	ND<100	ND<2.0	-	-

[1] Shaw modified CRRELanalysis
A= sample duplicate (B)=triplicate (C)=quadruplicate
B= Core Bottom
Q= Elevated reporting Limit
J = Estimated result. Result is less than reporting limits.
JS = Estimated result. Surrogate recovery is outside stated control limits and reanalysis was outside hold time.
JM = Estimated result. MS/MSD recovery is outside stated control limits.
JB = Estimated result. Method blank contains contamination.
ND = Not detected at the specified method detrection limit
NA = Not analyzed or not applicable
+ = Detected
- = Not detected
+- = Possible detection; slight coloration, but difference from blank color was inconclusive

Table 3-11. NC/NG Results for Concrete Expansion Joint Material

Sample Identification	Matrix	CRREL RDX Method Analyzed NC/NG Concentration of Associated Concrete as NC (mg/kg)	Modified CRREL Method Estimated NC/NG Concentration of EJM as NC[a] (mg/kg)
1885-01-CM-036-EJM	EJM	ND<100	ND<50
1890-01B-CM-042-EJM	EJM	ND<100	132
1890-01B-CM-046-EJM	EJM	124, 128	128
1885-03S-CM-049-EJM	EJM	ND<100	90
1885-03-CM-053-EJM	EJM	ND<100	ND<50
1885-02-CM-064-EJM	EJM	ND<100	ND<50

[a]Values are estimates because calibration was performed with background concrete extract matrix.
ND = Not detected at the specified estimated detection limit.

3.2.8 Data Assessment Summary

The data provided in Table 3-12 should be used to define the method performance capabilities for the CRREL RDX method for analysis of NC/NG on samples of the matrices tested.

Table 3-12

CRREL RDX Method Performance Metrics for NC/NG Analysis

Matrix (Test Group)	NG STL 8330 Detection Limit (mg/kg)	NC STL 353.2 Detection Limit (mg/kg)	CRREL RDX Detection Limit (NC) (mg/kg)	Test Sample Analysis Performance Indicators				
				%RPD Mean	%RPD STD	%False Positive	%False Negative	LR R Value
Wood	0.5 - 10	10-200	NA	NA	NA	NA	NA	NA
Soil	0.5	2.0-400	25	82.7	81.8	**2.7**	37.8	0.8979
Concrete	0.5	2.0-20	100	42.2	40.0	**2.4**	12.2	0.2196
Performance Criteria	3.6	NA	NA	NMT 20%	NA	NMT 10%	NMT 5%	≥0.95

NMT = not more than
RPD = relative percent difference
STD = standard deviation
NC = not calculated due to insufficient data points for correlation
NA = not applicable, wood only analyzed by Modified CRREL method

These data provided in Table 3-13 should be used to define the method performance capabilities for the Modified CRREL method for analysis of NC/NG on samples of the matrices tested.

Table 3-13

Modified CRREL Method Performance Metrics for NC/NG Analysis

Matrix (Test Group)	NG STL 8330 Detection Limit (mg/kg)	NC STL 353.2 Detection Limit (mg/kg)	Modified CRREL Detection Limit (NC) (mg/kg)	Test Sample Analysis Performance Indicators				
				%RPD Mean	%RPD STD	%False Positive	%False Negative	LR R Value
Wood	0.5 - 10	10-200	10-15	89.1	69.9	**0**	18.9	0.708
Soil	0.5	2.0-400	1.5	82.7	72.0	**0**	32.3	**0.9548**
Concrete	0.5	2.0-20	100	NA	NA	NA	NA	NA
Performance Criteria	3.6	NA	NA	NMT 20%	NA	NMT 10%	NMT 5%	≥0.95

NMT = not more than
RPD = relative percent difference
STD = standard deviation
NC = not calculated due to insufficient data points for correlation
NA = not applicable, wood only analyzed by Modified CRREL method

3.2.9 CRREL Method Conclusions

Findings from the field demonstration are as follows:

- The CRREL RDX method of analysis gives a relatively low response for NC compared to NG that is easily impacted by matrix interferences. Modifications to the CRREL RDX procedure to replace the acidic hydrolysis step with an alkaline hydrolysis greatly increased the method response for NC and retained the response for NG. The increase in response made the method more robust for NC analysis and allowed analysis of NC on the three sample matrices. The NC/NG response ratio obtained with the Shaw Modified CRREL method for NC/NG was close to the desired theoretical value of 1.31 based on the N content of each compound. It is Shaw's opinion that the CRREL RDX method is not appropriate for analysis of NC, especially in the matrix samples used in this study, and the Modified CRREL method is more suitable. With the limited amount of experience Shaw has with use of the Modified CRREL method since its development it appears to perform well for NC analysis providing low detection limits and predictable response.

- Tests conducted with NC on concrete showed that recovery of NC from the matrix was a function of both time and the manner in which NC was deposited on the matrix. Acetone solutions containing dissolved NC provided intimate contact of NC with the matrix when spiked onto concrete and only 10% of the initially recoverable NC was recovered after four hours by CRREL analysis. When NC was spiked onto concrete in the form of particulate material in an aqueous suspension approximately one-third was recovered after 96 hours. These results were attributed to decomposition of NC by the concrete matrix due to its alkaline nature in a similar manner as to what was concluded for NG in the bench test. The instability of NC/NG compounds on concrete matrix makes analysis difficult not only due to the potential impact on samples during handling and preparation, but also due to the effect on matrix standards.

- Compound detection performance metrics for NC/NG using the CRREL methods were not met for the three matrices (wood, soil, and concrete) tested during the field demonstration. False positives with both the CRREL RDX and the Modified CRREL method were less than 5 percent. False negatives, however, were greater than 10 percent for both CRREL methods and all three matrices, ranging from 12.2 percent to 37.8 percent. Performance metrics for concrete samples were limited by the number of positive results obtained by the CRREL methods.

  It is possible that the number of false negatives was elevated because NC was biased high by the STL Method 353.2 at low concentrations. An indication of this was provided by positive responses for NC in a number of the method blanks (false positives) for wood and soil, which had the highest percentages of CRREL false negatives. The bench test results also showed that the STL MCAWW 353.2 results were consistently biased high, especially at lower NC concentrations and NC was detected in unspiked clean background samples.

- Compound concentration metrics with respect to RPD values were not met by either CRREL method with any of the three matrices sampled during the building investigation. CRREL results were consistently biased low in comparison to the STL reference method results. The RPD between CRREL and STL results ranged from 42.2 to 89.1 percent. However, the results for the Modified CRREL method on soil showed a linear regression correlation to the STL results with a coefficient (R^2) of 0.9548, which is above the 0.95 performance metric. Performance metrics for concrete samples were limited by the number of positive results obtained by the CRREL methods.

There was no clear indication of why the CRREL results were biased low compared to the STL results. Most likely reasons include the following:

- STL Method 353.2 results were biased high due to matrix interference or contamination phenomenon similar to what affected method blanks and results from the bench test.
- Additional matrix interference in samples over that in background material used for standard preparation that caused low response for the CRREL methods.
- A change in STL analysis conditions such that the applied matrix sample correction from the bench test produced values that were too high. The applied correction increased the STL Method 353.2 result by a factor of 1.5 to 2.0.

- There was considerable scatter in the RPD values for the method result comparisons and this was attributed to non-homogeneous sample material and sources of contamination. Contamination of building materials (concrete and wood) was likely concentrated on exposed surfaces of the material. It is probable that the sample particle size of about a quarter of an inch was not small enough to provide sufficient distribution of contaminated pieces for uniform sampling. Soil samples contained pieces of propellant material that made preparing a homogeneous sample difficult.
- Analysis of six (6) samples of concrete expansion joint material associated with concrete samples were analyzed separately for NC/NG by the Modified CRREL method and concentrations detected were consistent with concentrations for the associated concrete sample.
- One field chemist with experience wet chemistry techniques is required for onsite analysis by the CRREL methods. Instrument (visible spectrophotometer) costs are about $2,000. Sample analysis rate during the demonstration was about 3-5 samples per hour.
- No routine maintenance is required. There was no downtime during the demonstration. Check standards are analyzed every day before and after sample analyses and after every 10 samples. Percent down time is estimated at less than one (1) percent.
- Field colorimetric analysis requires electrical power (110v) and a stable environment during operation, but is portable and can be used under a wide variety of site conditions.
- Some hazardous materials are generated by the method primarily acetone solvent and aqueous acetone solutions. Due to time constraints samples and standards were returned to the Shaw Lab in Knoxville. The left-over acetone extracts (~4 liters) will be disposed of as hazardous waste.
- Minimal investigative-derived waste was generated during the project.

3.3 Quantitative Analysis for NG by GC/TID

3.3.1 Introduction

A field-capable gas chromatography (GC) instrument equipped with a thermionic ionization detector (TID) was used to analyze the prepared sample extracts for NG. This method is selective for NG and does not produce a response for NC. The configuration is the same as the unit that was used in the bench study. Following a simple extraction procedure, sample extracts are injected directly onto the GC column within a heated injection port. Analytical times varied by matrix and ranged from less than 6 minutes to 11 minutes.

This method is not applicable to the analysis of NC because NC is nonvolatile. In order for a compound to be analyzed by GC it needs to be volatilized into the gas phase. It is in the gas phase that the compound can be mobilized, transferred and separated in the column and subsequently transferred to the detector for analysis. In addition NC decomposes at temperatures below the detector temperature and therefore is not detectable.

Background sample material of each test matrix (remaining from the bench test) was spiked at concentrations of NG ranging from 2.0 mg/kg to 400 mg/kg and used as calibration standards. A calibration curve was developed using the calibration samples for each test group. Results were calculated based on these curves. Instrument performance was continuously monitored by reanalysis of standards before and after each test group or every 10 samples. A blank, LCS, and MS/MSD were extracted and analyzed for each 20 samples of each matrix evaluated.

Figure 3-16. SRI GC/TID

3.3.2 Instrumentation

The GC used was the SRI Instruments, Inc (SRI) Model 8610C equipped with a heated TID, a heated on column injection port, and an internal air compressor. Separations were performed on a metal Crossbond 100 percent dimethyl polysiloxane column (DB-1), 15 m x 0.53 mm inside diameter, 0.5 micrometer film thickness.

The SRI Model 8610C as shown in Figure 3-16 is a transportable unit designed for field use Manual injections were made directly on the column using a 10 µL glass syringe with an extra long (6.0-7.0 cm) syringe needle that was supplied by SRI. GC data were collected on a Dell Latitude laptop computer using Peak Simple data collection software. The software was provided with the instrument from SRI.

3.3.3 Method

Sample extractions were prepared for each sample using acetone. This was the same extraction used for the colorimetric testing of EXPRAY™ / DROPEX^{Plus} and the CRREL method. The extraction is described above in Section 2.5. Manual injections of 1 µL volumes of the acetone extracts were directly injected onto the GC using the following GC conditions which were optimized as part of the bench study.

Injection port temperature:	180°C
Detector temperature:	250°C
TID bead voltage:	-320 millivolts
Internal air compressor pressure:	7 pounds per square inch (psi) for carrier gas
	1 psi for make-up gas
GC oven temperature program:	95°C for 0.5 minutes
	20°C/min to 160°C
	160°C for 2 minutes
	40°C/min to 210°C-240°C
	210°C-240°C for up to 3.25 minutes

Using the internal air compressor for both carrier and make-up gas eliminated the need for a high pressure gas cylinder, which is beneficial for field applications.

The GC oven temperature program listed above was modified for the different sample matrices based on the level of non-target analytes detected. In concrete samples the presence of non-target analytes was minimal allowing the maximum oven temperature to be lowered to 210°C decreasing the overall analytical time to 5.75 minutes per sample. By contrast, wood samples contained high levels of non-target analytes necessitating the oven temperature be held at 240°C for 3.25 minutes yielding a total analytical time of 11.0 minutes per sample. In addition to longer analytical times, samples containing high levels of non-target compounds resulted in a more rapid reduction of sensitivity caused by loading of the injection end of the column. Therefore, when wood extracts were analyzed, instrument performance was tested more frequently by analyzing standards as often as every 5 sample injections. When the recovery of a standard fell to less than 80 percent of the expected concentration approximately 6 inches were removed from the injection end of the column to regain sensitivity.

Evaluation of clean-up procedures on the sample extracts prior to injection may result in an effective way to minimize the effects of non-target compounds leading to less instrument downtime and therefore increased efficiency. For example, the alumina column cleanup used in the CRREL method described above may provide a benefit.

A calibration curve for each sample matrix was generated in the field by spiking the background wood, soil and concrete samples obtained during the bench scale testing with NG. The concentration for NG in the test samples was calculated based on this curve.

3.3.4 Data Assessment

For comparison purposes, the results for the GC-TID analyses of the samples are summarized in Table 3-6 (Wood), Table 3-7 (Soil) and Table 3-8 (Concrete Material) along with results for the lab reference method, STL (SW-846) Method 8330. Results for sample analyses for each matrix were obtained using the corresponding method calibration curve as described above and are reported in the tables.

The relative percent difference (RPD) between the reference method values (sample results) and the field method concentration have been calculated and tabulated in the summary along with the mean and standard deviation of the RPD. Non-detect (ND) results were set at the detection limit for this comparison except when non-detects were obtained for both methods and the non-detect levels were not similar. In this case the sample results were not included in the comparison analysis. If a positive result by one method was significantly lower than a non-detect level in the other method, these results were also excluded from the comparison analysis. The RPD data

provide a measure of the agreement between reference method results and the field method results to aid in method comparison. The RPD measures the analytical bias of the GC/TID results compared to the STL method results for the data set, and the standard deviation is a measure of scatter in the agreement between the method results for the data set.

In addition, for each matrix a linear regression plot was generated of the GC/TID sample results versus the reference Method 8330 results. The linear regression coefficient (R^2) values for each data set are also tabulated in the tables below. This provides another measure of the agreement of field method sample results with Method 8330 values.

Results for each sample matrix are discussed separately below. All samples were analyzed on site with the exception of the last soil samples collected, (sample numbers 82 through 99) which were returned to the Shaw Lab in Knoxville for analysis due to time constraints for the field demonstration.

Wood

Analysis results for NG on the wood samples by GC-TID are shown in Table 3-14 along with STL reference (SW-846 Method 8330) results for sample splits.

The detection limit for the GC/TID analysis of wood samples was 5 mg/kg NG. Twenty-four of the 37 samples evaluated had no detectable levels above the Method 8330 or GC/TID reporting limits. Detection limits for SW-846 Method 8330 results ranged from 0.5 to 10 mg/kg due to dilutions required because of matrix interference. Field method values for the samples with detectable concentrations (above 5 mg/kg NG) were an average of 62 percent lower than results from the STL 8330 reference method. For this set of data the average relative percent difference (RPD) was 89.9 percent and the standard deviation was 52.4 percent. For the entire data set, which includes non-detect results, the mean of the method percent differences was 48.7 percent and the standard deviation of the method percent differences was 53.0 percent. The data indicates there was a detectable negative bias to the GC/TID results. A correspondence plot of the GC/TID values and the STL 8330 value is shown on Figure 3-17 for the 13 wood samples with detectable values for NG.

The reason for the negative or high bias indicated by the field demonstration results is not known. Bench scale test results (as shown below) for NG spiked wood for STL Method 8330 and GC/TID correlated very well (R^2 = 0.985) with the NG spike concentration with no detectable bias. An average RPD of -2.3 percent and standard deviation of 14.9 percent were within performance metrics. A plot of the bench scale test NG spiked wood sample data is shown below in Figure 3-18 for comparison purposes.

Figure 3-17

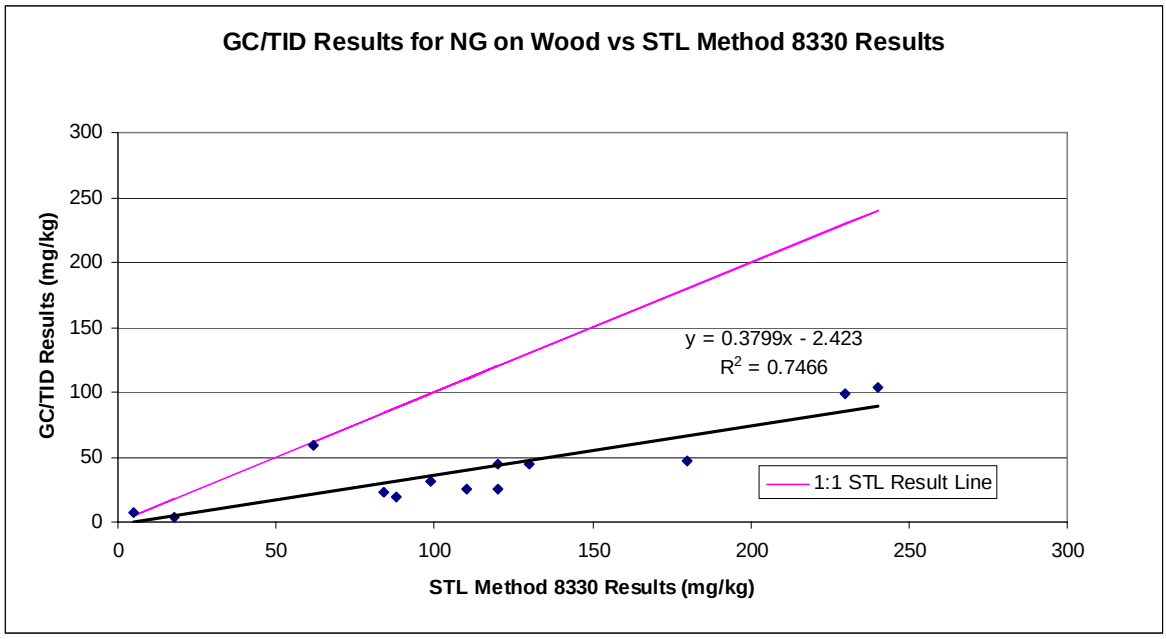
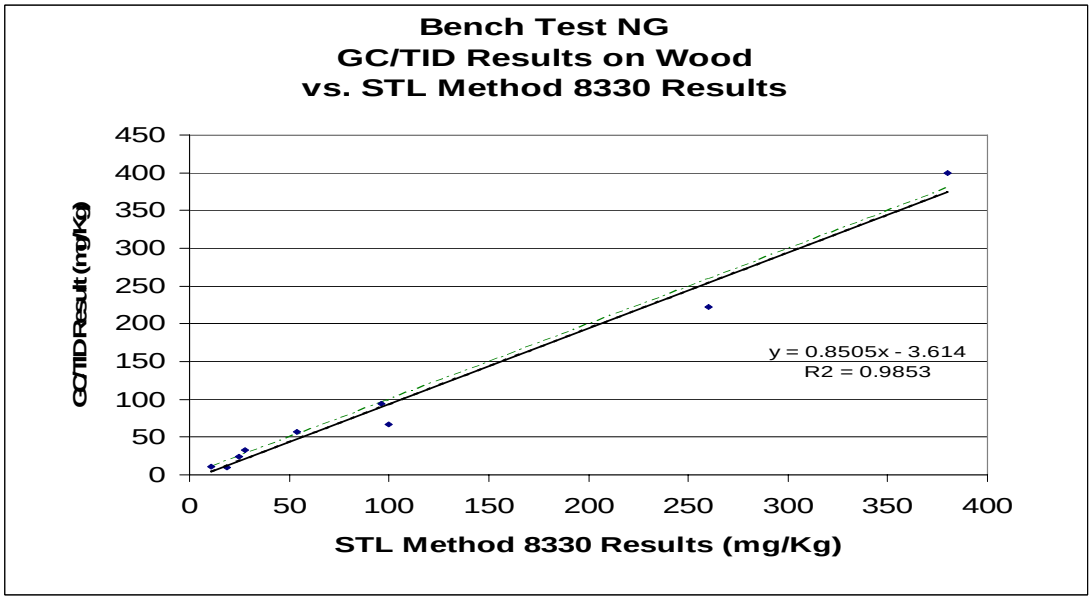


Figure 3-18



The bias in the field demonstration samples is thought to be matrix related. Ten (10) of the 13 samples with detectable concentrations were from the same building: 6709-17 pre-drying house. GC/TID field analysis included NG spiked MS/MSD samples for 6709-17-WD-019 and 1890-01-WD-022. Percent recovery for the MS/MD samples at 86%, 97% and 101%, 85%, respectively was within the method control limits (75%-125%. Method 8330 MS/MSD percent recovery for sample 6709-17-WD-012 was 38% and 137%, outside of method control limits (74%-112%). Sample 1890-01-WD-023 MS/MSD percent recovery was within limits at 87%, 89% respectively.

The percent of false negatives and false positives at 0 and 2.7, respectively, indicate general agreement between methods with regard to detection and non-detection; however, both the linear regression (LR) correlation coefficient (R^2 value) and RPD do not meet performance metrics of greater than 0.95 and not more than (NMT) 20 percent for the field demonstration samples.

Table 3-14. GC/TID Results for Wood Samples

Sample Identification	STL Reference Method Method 8330 Results NG Concentration mg/Kg	NG GC/TID Results NG Concentration mg/Kg
6657-02N-WD-001	3.7	ND<5.0
6657-02N-WD-002	18	3.2
6657-02I-WD-003	ND<0.5	ND<5.0
6657-02I-WD-003A	ND<5	ND<5.0
6657-02I-WD-004	ND<0.5	ND<5.0
5024-000-WD-005	ND<5	7.7
5024-000-WD-006	ND<5	ND<5.0
5024-000-WD-007	ND<5	ND<5.0
5024-000-WD-008	ND<5	ND<5.0
5024-000-WD-009	ND<0.5	ND<5.0
5024-000-WD-010	ND<5	ND<5.0
5024-000-WD-011	ND<2.5	ND<5.0
6709-17-WD-012	99	31.6
6709-17-WD-013	88	19.2
6709-17-WD-014	230	98.3
6709-17-WD-015	240	104
6709-17-WD-016	180	47.3
6709-17-WD-017	130	44.5
6709-17-WD-018	84	22.9
6709-17-WD-019	120	44.5
6709-17-WD-020	110	25.4
6709-17-WD-020A	120	25.9
6709-17-WD-021	62	58.5
1890-01-WD-022	ND<0.5	ND<5.0
1890-01-WD-023	ND<0.5	ND<5.0
1890-01-WD-024	ND<0.5	ND<5.0
1890-01-WD-025	ND<0.5	ND<5.0
1890-01-WD-026	ND<0.5	ND<5.0
1890-01-WD-027	ND<5	ND<50
1890-01-WD-028	ND<5	ND<5.0
1890-01-WD-028A	ND<5	ND<5.0
1890-01-WD-029	ND<5	ND<5.0
1890-01-WD-030	ND<5	ND<5.0
9590-000-WD-031	ND<0.5	ND<5.0
9590-000-WD-032	ND<10	ND<50
5024-000-WD-033	ND<0.5	ND<20
5024-000-WD-033A	ND<0.5	ND<20

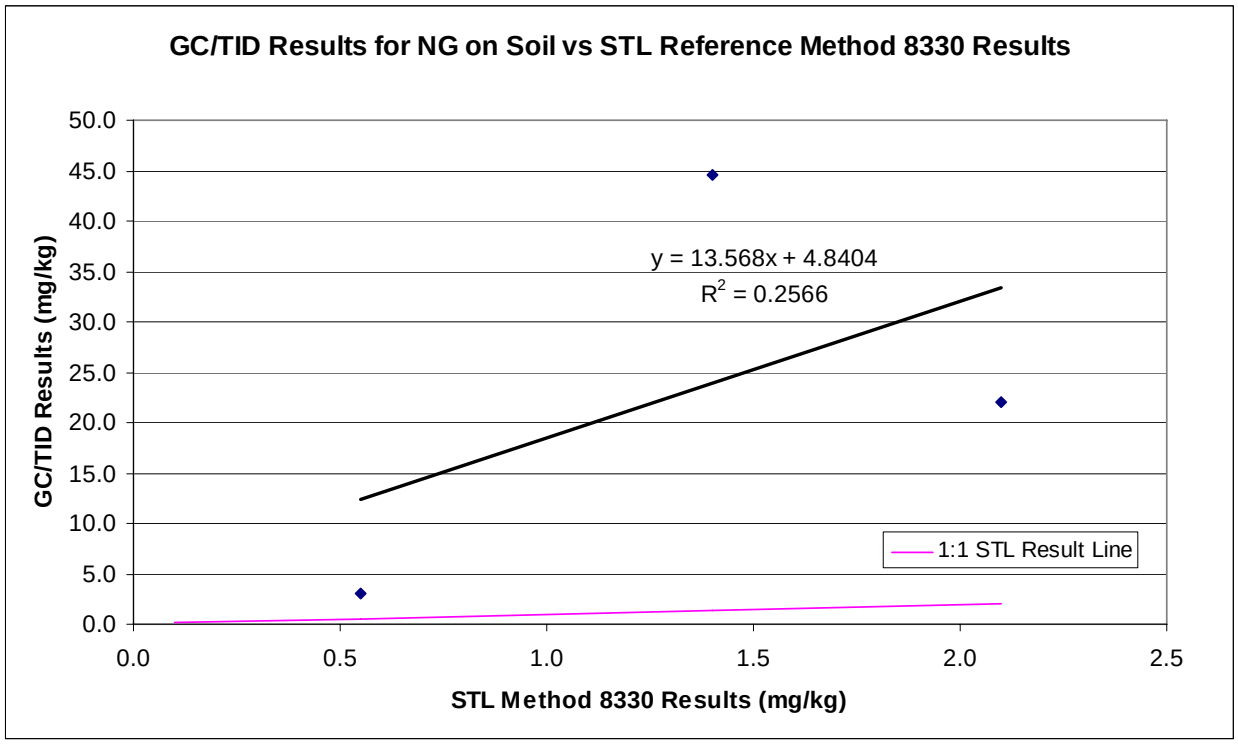
ND = Not detected at the specified method detrection limit
NA = Not analyzed or not applicable

Soil

Analysis results for NG on the soil samples by GC-TID are shown in Table 3 15 along with STL reference (SW-846 Method 8330) results for sample splits.

The detection limit for the GC/TID analysis of soil samples was 2.0 mg/kg NG. Detection limit for SW-846 Method 8330 was 0.5 mg/kg. The RPD for the entire data set including non-detects was -12.9 percent with a standard deviation of 45.4 percent. A plot of the GC/TID values and the STL 8330 value is shown in Figure 3-19 for the three soil samples with detectable values of NG. The average RPD for these three results was -163 percent and the standard deviation was 25.2 percent. This data indicates a positive bias for the GC/TID results above the detection limit compared to the STL results with the GC/TID result being on the average ten times the value obtained by the STL reference method.

Figure 3-19



Data from the bench scale test for GC/TID and STL Method 8330 correlated very well with the spike concentration with no detectable bias to the results. Samples collected for the field demonstration did not have significant NG contamination and did not provide enough data to obtain a good evaluation of data correlation.

The percent of false negatives and false positives at 2.7 and 5.4, respectively, as well as the average RPD for the entire data set of -12.9 percent indicate general agreement between methods with regard to detection and non-detection. However, the linear regression correlation coefficient (R^2) and average RPD (-163%) for the results above of the detection limit do not meet performance metrics of greater than 0.95 and not more than 20 percent for the field demonstration samples. These metrics are based on three results, which are not significantly above the detection limit, however, and it is felt they do not provide sufficient data and data of high enough quality to base a meaningful evaluation.

Table 3-15. GC/TID Results for Soil Samples

Sample Identification	STL Reference Method Method 8330 Results NG Concentration mg/Kg	NG GC/TID Results NG Concentration mg/Kg
1885-02-SS-067	ND<0.5	ND<2.0
1885-02-SS-068	0.55	ND<2.0
1885-02-SS-069	0.36	ND<2.0
1885-02-SS-070	ND<0.5	ND<2.0
1885-02-SS-071	ND<0.5	ND<2.0
1885-02-SS-072	2.1	22.0
1885-02-SS-072A	1.4	44.5
1885-02-SS-073	ND<0.5	ND<2.0
1885-03-SS-074	ND<0.5	ND<2.0
1885-03-SS-075	ND<0.5	ND<2.0
1885-03-SS-076	ND<0.5	ND<2.0
1885-03-SS-077	ND<0.5	ND<2.0
1885-03-SS-078	ND<0.5	ND<2.0
1890-01B-SS-079	ND<0.5	ND<2.0
1890-01B-SS-080	0.55	3.0
1890-01B-SS-081	ND<0.5	ND<2.0
1890-01B-SS-081A	ND<0.5	ND<2.0
1890-01B-SS-081B	NA	NA
1890-01B-SS-081C	NA	NA
1885-02-SS-082	1.0	ND<2.0
1885-02-SS-083	3.0	ND<2.0
1885-02-SS-083A	ND<0.5	ND<2.0
1885-02-SS-084	ND<0.5	ND<2.0
1885-02-SS-085	0.19	ND<2.0
1885-02-SS-086	ND<0.5	ND<2.0
1885-02-SS-087	0.82	ND<2.0
1885-02-SS-088	0.39	ND<2.0
1885-02-SS-089	ND<0.5	ND<2.0
1885-02-SS-090	ND<0.5	ND<2.0
1885-02-SS-091	ND<0.5	ND<2.0
1885-02-SS-092	ND<0.5	ND<2.0
1885-02-SS-093	0.18	ND<2.0
1885-02-SS-093A	ND<0.5	ND<2.0
1885-02-SS-094	ND<0.5	ND<2.0
1885-02-SS-095	ND<0.5	ND<2.0
1885-02-SS-096	ND<0.5	ND<2.0
1885-02-SS-097	ND<0.5	ND<2.0
1885-02-SS-098	ND<0.5	ND<2.0
1885-02-SS-099	ND<0.5	ND<2.0

ND = Not detected at the specified method detrection limit
NA = Not analyzed or not applicable

Concrete Material

In the bench test, calibration could not be performed with NG on concrete material and this was attributed to decomposition of NG by the concrete due its alkaline nature (See the discussion in the CRREL concrete results section 3.2.7). In the field demonstration concrete standards were spiked and analyzed immediately to minimize the time NG spent on the matrix and this procedure was successful in allowing a calibration for NG on concrete to be obtained. The GC/TID calibration response for NG on concrete was similar to that for NG on soil, so there was little adverse effect due to the matrix.

Analysis results for NG on the concrete samples by GC-TID are shown in Table 3-16 along with STL reference (SW-846 Method 8330) results for sample splits. There were only three samples with detectable amounts of NG by the STL reference method and they were; 1890-01B-CM-045, 1890-01B-CM-046 and its duplicate, 1890-01B-CM-046A. Two of these were the only samples that had detectable levels of NG by the GC/TID method and they were 1890-01B-CM-046 and its duplicate, 1890-01B-CM-046A. None of these results exceeded the NG cleanup criterion of 3.6 mg/kg. The values were near the method detection limits for both methods. The detection limit for the GC/TID analysis of concrete samples was 2.0 mg/kg NG. Detection limits for SW-846 Method 8330 was 0.5 mg/kg.

The RPD for the entire data set including non-detects was -4.4 percent with a standard deviation of 19.5 percent. The RPDs for the two samples with positive results by both methods were -78 percent and -103 percent. The GC/TID results were high compared to the STL results, but due to the low levels near the detection limits, and the increased analytical variability at these levels, the results are not considered to be of high enough quality to base a comparison.

The percent of false negatives and false positives at 0.0 and 4.9, respectively, as well as the average RPD for the entire data set of -4.4 percent indicate general agreement between methods with regard to detection and non-detection.

Table 3-16. GC/TID Results for Concrete Material Sample

Sample Identification	STL Reference Method Method 8330 Results NG Concentration mg/Kg	NG GC/TID Results NG Concentration mg/Kg
9590-000-CM-034	ND<0.5	ND<2.0
9590-000-CM-034A	ND<0.5	ND<2.0
1885-01-CM-035	ND<0.5	ND<2.0
1885-01-CM-035B	NA	ND<2.0
1885-01-CM-036	ND<0.5	ND<2.0
1885-01-CM-037	ND<0.5	ND<2.0
1890-01B-CM-038	ND<0.5	ND<2.0
1890-01B-CM-039	ND<0.5	ND<2.0
1890-01B-CM-040	ND<0.5	ND<2.0
1890-01B-CM-041	ND<0.5	ND<2.0
1890-01B-CM-042	ND<0.5	ND<2.0
1890-01B-CM-043	ND<0.5	ND<2.0
1890-01B-CM-043A	ND<0.5	ND<2.0
1890-01B-CM-044	ND<0.5	ND<2.0
1890-01B-CM-045	0.23J	ND<2.0
1890-01B-CM-046	1.1	2.52
1890-01B-CM-046A	0.46J	1.44
1885-03S-CM-047	ND<0.5	ND<2.0
1885-03S-CM-048	ND<0.5	ND<2.0
1885-03S-CM-049	ND<0.5	ND<2.0
1885-03S-CM-050	ND<0.5	ND<2.0
1885-03-CM-051	ND<0.5	ND<2.0
1885-03-CM-052	ND<0.5	ND<2.0
1885-03-CM-053	ND<0.5	ND<2.0
1885-03-CM-054	ND<0.5	ND<2.0
1885-03-CM-055	ND<0.5	ND<2.0
1885-03-CM-056	ND<0.5	ND<2.0
1885-02-CM-057	ND<0.5	ND<2.0
1885-02-CM-058	ND<0.5	ND<2.0
1885-02-CM-059	ND<0.5	ND<2.0
1885-02-CM-060	ND<0.5	ND<2.0
1885-02-CM-061	ND<0.5	ND<2.0
1885-02-CM-062	ND<0.5	ND<2.0
1885-02-CM-063	ND<0.5	ND<2.0
1885-02-CM-064	ND<0.5	ND<2.0
1885-02-CM-065	ND<0.5	ND<2.0
1885-02-CM-066	ND<0.5	ND<2.0
1885-02-CM-100	ND<0.5	ND<2.0
1885-02-CM-100A	ND<0.5	ND<2.0
1885-02-CM-100B	NA	ND<2.0
1885-02-CM-101	ND<0.5	ND<2.0
1885-02-CM-102	ND<0.5	ND<2.0
1885-02-CM-103	ND<0.5	ND<2.0

Q= Elevated reporting Limit
J = Estimated result. Result is less than reporting limits.
JS = Estimated result. Surrogate recovery is outside stated control limits and reanalysis was outside hold time.
JM = Estimated result. MS/MSD recovery is outside stated control limits.
JB = Estimated result. Method blank contains contamination.
ND = Not detected at the specified method detrection limit
NA = Not analyzed or not applicable

3.3.5 Summary of GC/TID Performance Metrics

The GC/TID field demonstration analysis performance parameters are summarized below in Table 3-17 for the matrix test groups.

Table 3-17. GC-TID Performance Metrics for NG Analysis

Matrix (Test Group)	STL 8330 Detection Limit (mg/kg)	GC/TID Detection Limit (mg/kg)	Test Sample Analysis Performance Indicators				
			%RPD Mean	%RPD STD	%False Positive	%False Negative	LR R Value
Wood	0.5 - 10	5	48.7	53.0	**2.7**	**0**	0.7466
Soil	0.5	2.0	**-12.9**	45.3	**5.4**	**2.7**	0.257
Concrete	0.5	2.0	**-4.43**	19.5	**4.9**	**0**	NC[1]
Performance Criteria	3.6	3.6	NMT 20%	NA	NMT 10%	NMT 5%	≥0.95

NMT = not more than
RPD = relative percent difference
STD = standard deviation
[1] NC = not calculated due to insufficient data points for correlation

3.3.6 GC/TID Method Conclusions

Findings from the field demonstration are as follows:

- Analyte detection performance metrics for NG were met for all three matrices (wood, soil, and concrete) tested during the field demonstration with <5 percent false negatives and <10 percent positives.
- Analyte concentration performance metrics for NG by GC/TID were not met with any of the three matrices sampled during the building investigation. The linear regression correlation coefficient (R^2) and average RPD for the results above of the detection limit do not meet performance metrics of greater than 0.95 and not more than 20 percent for the field demonstration samples.
- GC/TID analysis of NG on soil, and concrete samples was sensitive; a detection limit of 2 mg/kg, which was comparable to the reference method, was observed. Wood had a slightly higher detection limit of 5 mg/kg.

- Thirteen (13) of the 37 wood samples evaluated had positive values for NG by the 8330 reference method for comparison. The GC/TID results were low in comparison with values that averaged 38.0 percent of the STL values. This bias was not observed during the bench scale testing. Matrix interference with the STL Method 8330 results is a possible explanation but is unconfirmed. The analysis report by STL indicated that many samples required dilution due to matrix interferences and surrogates were diluted out preventing evaluation. Evaluation of matrix related QC samples was also inconclusive

- Soil sample results by GC/TID were possibly biased high; however, there was insufficient NG contamination in the field demonstration samples collected to effectively evaluate performance. The thirteen samples containing detectable amounts of NG by STL Method 8330 had concentrations ranging from 0.18 to 3.0 mg/k and these are right around the method detection limit of 0.5 mg/kg where analytical variability is the greatest (four values were estimates below the detection limit).

- Concrete sample results by GC/TID were possibly biased high; however, there was insufficient NG contamination in the samples collected in the field demonstration to effectively evaluate performance. Only one sample contained NG above the 8330 method detection limit of 0.5 mg/kg. The GC/TID method also gave only one result above the detection limit of 2 mg/kg. It is believed that NG is not stable in the alkaline concrete matrix.

- In general, reliability of the GC/TID ability to detect NG on the building materials was consistent with the reference Method 8330. Both methods may be subject to matrix interference effects and QC samples should be included to help assess data quality.

- One field chemist with experience in gas chromatography is required for onsite analysis by GC/TID. Instrument costs are about $10,000 and do not require the use of compressed gases. Sample analysis rate during the demonstration was about 3-5 samples per hour

- Minimal routine GC maintenance (septa replacement, cutting column) is required. There was relatively little downtime during the demonstration. Maintaining sensitivity required frequent cutting of the injection end of the column. The frequency is matrix dependent and thought to be due to loading or degradation of the column material by non-target constituents in the sample. This problem was most prevalent with the wood samples. Check standards are analyzed frequently; every 10 samples for soil and concrete, every 5 samples for wood, to monitor loss of sensitivity. Percent down time was estimated at 5-7 percent.

- Field GC/TID analysis requires electrical power (110v) and a stable environment during operation, but is portable and can be used under a wide variety of site conditions.

- Minimal hazardous materials were generated by the method. Due to time constraints samples and standards were returned to the Shaw Lab in Knoxville. The left-over acetone extracts (~2 liters) will be disposed of as hazardous waste.

- Minimal investigative-derived waste was generated during the project.

4.0 SUMMARY OF METHOD CONCLUSIONS

During the field demonstration three field analytical methodologies were evaluated for identifying and/or quantifying nitrocellulose (NC) and nitroglycerine (NG) in soils as well as wood and concrete building materials collected at Badger Army Ammunition Plant (BAAAP) in Baraboo, WI. This was accomplished by analysis of acetone extracts of soils, concrete material, and wood samples by each of the on-site methods and results compared to off-site laboratory analysis of sample splits using high performance liquid chromatography (HPLC) with EPA SW-846 Method 8330 for NG and MCAWW Method 353.2 for NC, a chemical treatment and adapted automated colorimetric method. The field methods evaluated included EXPRAY™ and DROPEX^{Plus} colorimetric test kits (qualitative for total NC/NG), and the following quantitative methods: CRREL RDX colorimetric test (proposed EPA SW-846 8510) for total NC/NG and GC/TID field gas chromatograph for NG only. EXPRAY™ and DROPEX^{Plus} analyses that were evaluated were performed on sample extracts. Surface wipe analyses with DROPEX^{Plus} only were performed on concrete core samples prior to extraction. Accuracy of the qualitative methods was evaluated based on percent false positive / false negatives. The quantitative on-site methods were evaluated using linear regression analysis and relative percent difference (RPD) comparison criteria. General comments as well as major findings from the field demonstration are summarized below for each of the three technologies evaluated; more detailed discussions are included in the respective technology sections.

General Comments

The field methods can be implemented as quantitative detection tools depending on the method performance requirements for use. The data quality objectives including the required method detection/quantitation limits and precision and accuracy for the intended use need to be established before use can be assessed. If NC concentrations need to be quantitated below about 50 mg/kg then the STL MCAWW reference method is not usable for the matrices studied whereas the modified CRREL field method may be usable. For concentrations above about 50 mg/kg either method should be usable providing the requirements for precision and accuracy can be demonstrated. Further development may be needed on sample preparation of these sample matrices to obtain an aliquot for analysis that is representative and produces consistent results before precision and accuracy can be assessed.

The concrete matrix presents an issue for validation and use of the methods. Since the analytes are not stable on the matrix, the analysis needs to use standards and spikes prepared in matrix extract solutions rather than spiked matrix samples. This will be an issue regardless of the analytical method used.

DROPEX^{Plus}/EXPRAY™

- DROPEX^{Plus} analysis of concrete core samples by surface wipes yielded more positive results (10 positives) than the sample extract analyses (2 positives) and suggested increased sensitivity was observed because contamination was concentrated on the sample surface.

- EXPRAY™ was effective in detecting NC and NG in the matrices with results consistent with the STL 8330/8332 reference method as long as concentrations were above detectable limits.

- DROPEX^{Plus} did not meet the performance metrics for wood or soil. This was likely due to lower detection limits, which involved more samples with concentrations near the detection limit where variability in method performance is the highest and has the greatest impact.

- EXPRAY™ tests, while slightly less sensitive, was easier to evaluate as either detect or non-detect. DROPEX^{Plus} when applied seemed to spread out more and had more prevalent yellow discoloration. With both applications only an immediate and distinct color change should be considered to be a positive result. If the collection paper is left exposed, once reagents have been applied, it is possible for a color change to occur after a given amount of time due to pollutants or contaminants present in the ambient air.

- Both the EXPRAY™ and DROPEX^{Plus} field kits are easy to use with little specialized training and equipment. Each kit contains reagents for 200 tests. Cost of each EXPRAY™ kit is $240 and contains reagents for 100 tests. Cost of each DROPEX^{Plus} kit is $190 and contains reagents for 50 tests.

- Overall EXPRAY™ / DROPEX^{Plus} is thought to be a useful tool for screening the presence of significant concentrations of NC and or NG (0.1 to 1 percent and above) in the field or on sample extracts. Given its relatively low rate of false negative results, in combination with other field methods it could be a beneficial screening tool for identifying areas that do not contain explosive contamination in buildings within specified limits. Detectable levels are matrix dependent, with low confidence in results at or near the detection limit. The field method should only be used as a screening tool in combination with other supportive methods of analysis. During the bench test portion of testing the performance of both of these field kit technologies was not affected by the cold temperature when used at 4°C.

CRREL Method for NC/NG

- The CRREL RDX method of analysis gives a relatively low response for NC compared to NG that is easily impacted by matrix interferences. Modifications to the CRREL RDX procedure greatly increased the method response for NC and retained the response for NG. The increase in response made the method more robust for NC analysis and allowed analysis of NC on the three sample matrices. It is Shaw's opinion that the CRREL RDX method is not appropriate for analysis of NC, especially in the matrix samples used in this study, and the Modified CRREL method is more suitable. With the limited amount of experience Shaw has with use of the Modified CRREL method since its development it appears to perform well for NC analysis providing low detection limits and predictable response.

- Tests conducted with NC on concrete showed that recovery of NC from the matrix was a function of both time and the manner in which NC was deposited on the matrix. Acetone solutions containing dissolved NC provided intimate contact of NC with the matrix when spiked onto concrete and only 10% of the initially recoverable NC was recovered after four hours by CRREL analysis. When NC was spiked onto concrete in the form of particulate material in an aqueous suspension approximately one-third was recovered after 96 hours. These results were attributed to decomposition of NC by the concrete matrix due to its alkaline nature in a similar manner as to what was concluded for NG in the bench test. The instability of NC/NG compounds on concrete matrix makes analysis

difficult not only due to the potential impact on samples during handling and preparation, but also due to the effect on matrix standards.

- Compound detection performance metrics for NC/NG using the CRREL methods were not met for the three matrices (wood, soil, and concrete) tested during the field demonstration. False positives with both the CRREL RDX and the Modified CRREL method were less than 5 percent. False negatives, however, were greater than 10 percent for both CRREL methods and all three matrices, ranging from 12.2 percent to 37.8 percent. Performance metrics for concrete samples were limited by the number of positive results obtained by the CRREL methods.

  It is speculated that the number of false negatives was elevated because NC was biased high by the STL Method 353.2 at low concentrations. An indication of this was provided by positive responses for NC in a number of the method blanks (false positives) for wood and soil, which had the highest percentages of CRREL false negatives. False positives at low concentrations were also obtained in the bench test results.

- Compound concentration metrics with respect to RPD values were not met by either CRREL method with any of the three matrices sampled during the building investigation. CRREL results were consistently biased low in comparison to the STL reference method results. The RPD between CRREL and STL results ranged from 42.2 to 89.1 percent. However, the results for the Modified CRREL method on soil showed a linear regression correlation to the STL results with a coefficient (R^2) of 0.9548, which is above the 0.95 performance metric. Performance metrics for concrete samples were limited by the number of positive results obtained by the CRREL methods.

  Most likely reasons why the CRREL results were biased low compared to the STL results include the following:

  - STL Method 353.2 results were biased high due to matrix interference or contamination phenomenon similar to what affected method blanks and clean background matrix analyses in the bench test.

  - Additional matrix interference in samples over that in background material used for standard preparation that caused low response for the CRREL methods.

  - A change in STL analysis conditions such that the applied matrix sample correction from the bench test produced values that were too high.

- There was considerable scatter in the RPD values for the method result comparisons and this was attributed to non-homogeneous sample material and sources of contamination. Soil samples in particular contained pieces of propellant material that made preparing a homogeneous sample difficult.

- Analysis of six (6) samples of concrete expansion joint material associated with concrete samples were analyzed separately for NC/NG by the Modified CRREL method and concentrations detected were consistent with concentrations for the associated concrete sample.

- One field chemist with experience wet chemistry techniques is required for onsite analysis by the CRREL methods. Instrument (visible spectrophotometer) costs are about $2,000. Sample analysis rate during the demonstration was about 3-5 samples per hour.

GC/TID Method for NG Conclusions

- Analyte detection performance metrics for NG were met for all three matrices (wood, soil, and concrete) tested during the field demonstration with <5 percent false negatives and <10 percent positives.

- Analyte concentration performance metrics for NG by GC/TID were not met with any of the three matrices sampled during the building investigation. The linear regression correlation coefficient (R^2) and average RPD for the results above of the detection limit do not meet performance metrics of greater than 0.95 and not more than 20 percent for the field demonstration samples.

- GC/TID analysis of NG on soil, and concrete samples was sensitive; a detection limit of 2 mg/kg, which was comparable to the reference method, was observed. Wood had a slightly higher detection limit of 5 mg/kg.

- Thirteen (13) of the 37 wood samples evaluated had positive values for NG by the 8330 reference method for comparison. The GC/TID results were low in comparison with values that averaged 38.0 percent of the STL values. This bias was not observed during the bench scale testing. Matrix interference with the STL Method 8330 results is a possible explanation but is unconfirmed.

- Soil sample results by GC/TID were possibly biased high; however, there was insufficient NG contamination in the field demonstration samples collected to effectively evaluate performance. The thirteen samples containing detectable amounts of NG by STL Method 8330 had concentrations ranging from 0.18 to 3.0 mg/k and these are right around the method detection limit of 0.5 mg/kg where analytical variability is the greatest (four values were estimates below the detection limit).

- Concrete sample results by GC/TID were possibly biased high; however, there was insufficient NG contamination in the samples collected in the field demonstration to effectively evaluate performance.

- In general, reliability of the GC/TID ability to detect NG on the building materials was consistent with the reference Method 8330. NG methods seem to perform well, but validation was hampered primarily by limited number of samples and sample non-homogeneity. Both methods may be subject to matrix interference effects and QC samples should be included to help assess data quality.

- One field chemist with experience in gas chromatography is required for onsite analysis by GC/TID. Instrument costs are about $10,000 and do not require the use of compressed gases. Sample analysis rate during the demonstration was about 3-5 samples per hour

- Maintaining sensitivity required frequent cutting of the injection end of the column. The frequency is matrix dependent and thought to be due to loading or degradation of the

column material by non-target constituents in the sample. This problem was most prevalent with the wood samples.

Method Performance Evaluations

A summary of accomplishment for each of each of the field methods investigated in the field demonstration is tabulated below for each of the building materials tested in Tables 4-1, 4-2 and 4-3.

Table 4-1 Wood Samples
Performance Evaluation against Primary and Secondary Criteria

Performance Criteria	Expected Performance Metric (pre-Demo)	Performance Confirmation Method	Actual Performance (post-Demo)
Primary Criteria			
Compound Identification	NMT 5% False Negatives NMT 10% False Positives (Applies to DROPEX^{Plus} / EXPRAY™)	Confirm by laboratory analysis. Data will be evaluated on agreement of detection.	• DROPEX^{Plus} Field Method False negatives=16.2% • EXPRAY™ Field Method False negatives= 0% • DROPEX^{Plus} Field Method False Positives= 5.4% • EXPRAY™ Field Method False Positives= 13.5% Field Method does not meet specified criteria
Compound Concentration	RPD NMT 20% and/or Correlation Coefficient ≥ 0.95 (Applies to CRREL and GC/TID)	Confirm by laboratory analysis. Data are evaluated on agreement of detection and concentration	• Mod. CRREL Field Method RPD=89.1 • GC/TID Field Method RPD= 48.7 • Mod. CRREL Field Method LR R value=0.7080 • GC/TID Field Method LR R value= 0.7466 Field Methods do not meet specified criteria
Reliability	Achieve identification and quantitation requirements in multiple locations and conditions	Confirm by laboratory analysis	• GC/TID- wood does not pass RPD criteria • CRREL/Mod. CRREL does not meet specified criteria

Ease of Use	Reduced or constant crew size. Level of technical training required. Need for special assistance or training during project. Calibration and maintenance can be performed by operating crew.	Experience from demonstration	• EXPRAY™/ DROPEX^{Plus} ® is easy to use with little specialized training and equipment. • CRREL requires a moderate level of training in regards to matrix • GC/TID requires specialized training

Wood Samples Table 4-1 (Cont.)

Performance Criteria	Expected Performance Metric (pre-Demo)	Performance Confirmation Method	Actual Performance (post-Demo)
Maintenance	Percent downtime when operations are scheduled. Routine maintenance required. Specialized personnel or equipment for maintenance activities.	Experience from demonstration	DROPEX^{Plus} / EXPRAY™ does not use equipment that requires maintenance or repair. CRREL does not use equipment that requires maintenance or repair. GC/TID maintenance and repair can be performed by trained GC analyst with 5-10% downtime
Secondary Criteria			
Versatility	Use conditions and ease of use under a variety of site conditions.	Experience from demonstration	DROPEX^{Plus} / EXPRAY™ can be used under a wide variety of site conditions CRREL can be used under a wide variety of site conditions GC/TID requires a relatively stable environment with temperatures within 70 ±20 degrees F All equipment is portable, light and easily transported

Wood Samples Table 4-1 (Cont.)

Performance Criteria	Expected Performance Metric (pre-Demo)	Performance Confirmation Method	Actual Performance (post-Demo)
Hazardous Materials	Volume of hazardous materials generated by project operations. Number of waste streams requiring characterization and disposal	Experience from demonstration	• Minimal hazardous materials were generated during project. • Remaining acetone extracts were returned to Shaw Knoxville Lab for disposal as hazardous waste
Process Waste	Amount of investigative-derived waste generated by project operations.	Experience from demonstration	Minimal investigation-derived waste was generated during the project

Notes:
NMT = not more than
RPD = Relative Percent Difference

Table 4-2 Soil Samples
Performance Evaluation against Primary and Secondary Criteria

Performance Criteria	Expected Performance Metric (pre-Demo)	Performance Confirmation Method	Actual Performance (post-Demo)
Primary Criteria			
Compound Identification	NMT 5% False Negatives NMT 10% False Positives (Applies to DROPEX^{Plus} / EXPRAY™)	Confirm by laboratory analysis. Data will be evaluated on agreement of detection.	• DROPEX^{Plus} Field method false negatives=10.8% • EXPRAY™ Field method false negatives= 2.7% • DROPEX^{Plus} Field Method False Positives= 16.2% • EXPRAY™ Field Method False Positives= 8.1% DROPEX^{Plus} does not meet criteria. EXPRAY™ does meet criteria.
Compound Concentration	RPD NMT 20% and/or Correlation Coefficient ≥ 0.95 (Applies to CRREL and GC/TID)	Confirm by laboratory analysis. Data are evaluated on agreement of detection and concentration	• Mod. CRREL Field Method RPD=82.7 • GC/TID Field Method RPD= -12.9 • Mod. CRREL Field Method R value=0.9548 • GC/TID Field Method LR R value= 0.2566
Reliability	Achieve identification and quantitation requirements in multiple locations and conditions	Confirm by laboratory analysis	• GC/TID- soil and concrete quantitation not confirmed because of absence of NG compound. • CRREL/Mod. CRREL does not meet specified criteria
Ease of Use	Reduced or constant crew size. Level of technical training required. Need for special assistance or training during project. Calibration and maintenance can be performed by operating crew.	Experience from demonstration	• EXPRAY™/ DROPEX^{Plus} ® is easy to use with little specialized training and equipment. • CRREL requires a moderate level of training in regards to matrix • GC/TID requires specialized training

Soil Samples Table 4-2 (Cont.)

Performance Criteria	Expected Performance Metric (pre-Demo)	Performance Confirmation Method	Actual Performance (post-Demo)
Maintenance	Percent downtime when operations are scheduled. Routine maintenance required. Specialized personnel or equipment for maintenance activities.	Experience from demonstration	DROPEX^{Plus} / EXPRAY™ does not use equipment that requires maintenance or repair. CRREL does not use equipment that requires maintenance or repair. GC/TID maintenance and repair can be performed by trained GC analyst with 5-10% downtime
Secondary Criteria			
Versatility	Use conditions and ease of use under a variety of site conditions.	Experience from demonstration	DROPEX^{Plus} / EXPRAY™ can be used under a wide variety of site conditions CRREL can be used under a wide variety of site conditions GC/TID requires a relatively stable environment with temperatures within 70 ±20 degrees F All equipment is portable, light and easily transported

Soil Samples Table 4-2 (Cont.)

Performance Criteria	Expected Performance Metric (pre-Demo)	Performance Confirmation Method	Actual Performance (post-Demo)
Hazardous Materials	Volume of hazardous materials generated by project operations. Number of waste streams requiring characterization and disposal	Experience from demonstration	• Minimal hazardous materials were generated during project. • Remaining acetone extracts were returned to Shaw Knoxville Lab for disposal as hazardous waste
Process Waste	Amount of investigative-derived waste generated by project operations.	Experience from demonstration	Minimal investigation-derived waste was generated during the project

Notes:
NMT = not more than
RPD = Relative Percent Difference

Table 4-3 Concrete Material
Performance Evaluation against Primary and Secondary Criteria

Performance Criteria	Expected Performance Metric (pre-Demo)	Performance Confirmation Method	Actual Performance (post-Demo)
Primary Criteria			
Compound Identification	NMT 5% False Negatives NMT 10% False Positives (Applies to DROPEX^{Plus} / EXPRAY™)	Confirm by laboratory analysis. Data will be evaluated on agreement of detection.	• DROPEX^{Plus} Field method false negatives=2.4% • EXPRAY™ Field method false negatives= 4.9% • DROPEX^{Plus} Field Method False Positives= 2.4% • EXPRAY™ Field Method False Positives= 0% DROPEX^{Plus} and EXPRAY™ meet performance criteria.
Compound Concentration	RPD NMT 20% and/or Correlation Coefficient ≥ 0.95 (Applies to CRREL and GC/TID)	Confirm by laboratory analysis. Data are evaluated on agreement of detection and concentration	• CRREL Field Method RPD=45.9 • GC/TID Field Method RPD= -4.43 • CRREL Field Method R value=0.0894 • GC/TID Field Method LR R value= NC insufficient data points. • CRREL and GC/TID fail to meet specified criteria
Reliability	Achieve identification and quantitation requirements in multiple locations and conditions	Confirm by laboratory analysis	• GC/TID- soil and concrete quantitation not confirmed because of absence of NG compound. • CRREL performance not confirmed

Ease of Use	Reduced or constant crew size. Level of technical training required. Need for special assistance or training during project. Calibration and maintenance can be performed by operating crew.	Experience from demonstration	• EXPRAY™/ DROPEX^{Plus} ® is easy to use with little specialized training and equipment. • CRREL requires a moderate level of training in regards to matrix • GC/TID requires specialized training

Table 4-3. Concrete Material (Cont.)

Performance Criteria	Expected Performance Metric (pre-Demo)	Performance Confirmation Method	Actual Performance (post-Demo)
Maintenance	Percent downtime when operations are scheduled. Routine maintenance required. Specialized personnel or equipment for maintenance activities.	Experience from demonstration	DROPEX^{Plus} / EXPRAY™ does not use equipment that requires maintenance or repair. CRREL does not use equipment that requires maintenance or repair. GC/TID maintenance and repair can be performed by trained GC analyst with 5-10% downtime
Secondary Criteria			

Versatility	Use conditions and ease of use under a variety of site conditions.	Experience from demonstration	DROPEX^{Plus} / EXPRAY™ can be used under a wide variety of site conditions CRREL can be used under a wide variety of site conditions GC/TID requires a relatively stable environment with temperatures within 70 ±20 degrees F All equipment is portable, light and easily transported

Table 4-3. Concrete Material (Cont.)

Performance Criteria	Expected Performance Metric (pre-Demo)	Performance Confirmation Method	Actual Performance (post-Demo)
Hazardous Materials	Volume of hazardous materials generated by project operations. Number of waste streams requiring characterization and disposal	Experience from demonstration	• Minimal hazardous materials were generated during project. • Remaining acetone extracts were returned to Shaw Knoxville Lab for disposal as hazardous waste
Process Waste	Amount of investigative-derived waste generated by project operations.	Experience from demonstration	Minimal investigation-derived waste was generated during the project

Notes:
NMT = not more than
RPD = Relative Percent Difference

5.0 COST ASSESSMENT

5.1 Cost Reporting

Project costs were tracked and the costs associated with the field demonstration are summarized in Table 5-1. These costs include those for planning, concrete drill fabrication/modification, lab trailer and generator rental, fuel for the lab trailer generator and on-site operations, personnel travel, on-site materials and supplies, shipping, off-site analytical and other subcontractor charges and labor for on-site sampling and analytical work as well as off-site (Knoxville) analytical method development work.

5.2 Cost Analysis

5.2.1 Cost Basis

The project costs from November 2005 through March of 2006 are directly related to the field demonstration and associated administrative activities and can be divided into five (5) cost categories:

1. On-site sampling
2. On-site sample analysis
3. Off-site sample analysis and data validation
4. Off-site method development/sample reanalysis, and
5. Administration and reporting

Administrative and reporting costs totaled $53,035 and are not included in Table 5-1. The costs for the field demonstration activities that are included in Table 5-1 totaled $176,264. The total project cost for the field demonstration including administrative and reporting activities was $229,299.

Sampling costs of $37,229 included sample design and planning, equipment fabrication (remote operated concrete drill, and sample crusher), materials and supplies related to sampling activities, equipment rental, personnel travel costs and labor for sampling activities. These costs can be used for estimating sampling costs, but they were affected by the sub-freezing temperatures, which necessitated special efforts to thaw soil for sampling beneath the concrete slab at concrete core sampling sites. A water-cooled, diamond tipped, hollow coring bit was used to drill through concrete floor slabs. This was chosen as a method to provide safe access to sub-slab samples. This method was expensive and likely caused some disturbance to the sample due to the water used to cool the drill bit. Alternative methods of obtaining these samples should continue to be investigated. Costs related to concrete cutting will also be affected by the thickness and strength of the concrete slab.

On-site sample analysis costs of $61,808 included those for planning, materials and supplies related to analyses, lab trailer and generator rental as well as associated delivery charges, generator fuel costs, personnel travel costs, shipping charges for equipment and supplies during mobilization and demobilization and labor for sample preparation and analysis. The costs are subdivided into the three analytical method technologies, i.e., EXPRAY™ / DROPEX^{Plus}, GC/TID and CRREL. The estimated cost breakdown for each method technology is $10,493 for EXPRAY™ / DROPEX^{Plus}, $24,078 for GC/TID and $27,237 for CRREL. These costs are for the analysis of the 115 samples; 103 field samples and 12 field sample duplicates.

Off-site sample analysis costs of $22,830 included those for sample shipping, unit price charges for samples analyzed by STL and costs for data validation. What are not included are labor costs for sample shipment and administrative activities as well as for sample preparation activities, which are included in on-site analytical charges. Sample preparation that was necessary for both on-site and off-site analyses was performed on-site during the analysis efforts and the costs are difficult to separate out accurately; however, they are estimated to be fifteen (15) percent of the estimated on-site analytical labor costs of $33,081or approximately $4,960. The off-site analysis costs plus the estimated sample preparation cost gives a total cost of $27,790 for the off-site analysis of the 115 field and field duplicate samples.

There was a significant effort expended after the on-site field demonstration at the TDL in Knoxville, TN for CRREL RDX method development/modification and sample re-analysis that would not be needed for routine use of the developed method. It was felt that the labor expended on site is a good estimate of the labor needed to complete the analysis of the samples collected for the field demonstration using the EXPRAY™ /DROPEX^{PLUS}, GC/TID and the developed Modified CRREL field methods. Therefore the off-site method development costs were not included with the costs for on-site analytical work. An estimate of the labor and materials cost for off-site CRREL method development has been separated from the on-site work and shown in a separate column in Table 5-1.

5.2.2 Cost Comparison

The off-site analytical laboratory (STL) costs for the demonstration samples of $27,790 (includes $4,960 cost for sample preparation) can be compared to the on-site analytical costs to assess cost effectiveness for on-site analyses. This comparison does not include administrative costs previously mentioned or the cost for expedited turnaround of results from the off-site lab that would be incurred to get a more direct comparison to the on-site field analysis. On-site analysis typically generates results the same day or within 24-48 hours. The off-site analyses were performed by STL with a three week turnaround time for results. STL typically charges a fifty (50) to one hundred (100) percent surcharge for results within a 24-48 hour turn around time. However, there is typically a 24 hour delay due to overnight shipping, so it is difficult for an off-site lab to duplicate the turn around time for results that an on-site lab can provide.

Another factor affecting the cost that should be considered for cost comparison is the experience level of the analysts used for field method analysis. Since this was a method evaluation and included analytical method development, the experience level and associated pay rate for analysts were higher than what would typically be used for field work using established analytical procedures.

It is difficult to get a clear cost comparison for the EXPRAY™ / DROPEX^{Plus} and CRREL methods to the off-site reference method analyses because the results for the methods are not equivalent. The CRREL method provides a total for NC and NG while EXPRAY™ and DROPEX^{Plus} are not quantitative and the MCAWW 353.2 reference method only quantifies NC. The estimated total cost for the GC/TID and CRREL analyses, which provide separate results for NG and NC (by difference between the CRREL total NC and NG result and the GC/TID NG result), was $51,315. This is approximately twice the cost for the off-site STL reference method analyses of $27,790 that provides separate results for NC and NG; however, the costs would be more comparable if expedited surcharges and less experienced field analysts impacts discussed above were considered. The GC/TID method and the STL 8330/8332 method both provide quantitative results for NG only and the estimated costs for these analyses were $24,078 and approximately $13,000, respectively. The on-site GC/TID cost was approximately twice that for

the off-site lab analysis and is consistent with the former comparison, but again lacks the considerations for a more valid comparison.

Table 5-1 Demonstration Costs

Cost Category	Sub Category	Details	Field Sampling	On-Site DROPEX^{Plus} / EXPRAY^{TM} Analysis	On-Site GC/TID Analysis	On-Site Modified CRREL Analysis	Off-Site CRREL Method Development	Off-Site STL Reference Method Analyses	Total Actual Demonstration Costs (Includes Shaw Costs)
Start-Up Costs	Site Characterization	N/A	$	$	$	$	$	$	$
	Mobilization	Project planning	$5,000	$2,500	$2,500	$2,500	$	$	$12,500
		Project coordination	$	$	$	$	$	$	$
		Personnel travel to site	$5,845	$3,333	$3,333	$3,334	$	$	$15,845
		Equipment travel to site	$	$	$	$	$	$	$
		Shipping costs	$483	$	$400	$400	$	$	$1,283
Capital Costs	Capital Equipment Purchase	N/A	$	$	$	$	$	$	$
	Ancillary Equipment Purchase	N/A	$	$	$	$	$	$	$
	Modifications	N/A	$940	$	$	$	$	$	$940
	Structures Installation	N/A	$	$	$	$	$	$	$
	Engineering	N/A	$	$	$	$	$	$	$
Operating Costs	Capital Equipment Rental	Shaw Rental	$	$402	$403	$403	$	$	$1,208
		N/A	$	$	$	$	$	$	$
		N/A	$	$	$	$	$	$	$
	Ancillary Equipment Rental	Generator/fuel	$	$380	$380	$381	$	$	$1,141
		Phone Services	$450	$96	$200	$200	$	$	$946
	Supervision	Salary	$	$	$	$	$	$	$
		Travel	$	$	$	$	$	$	$
		Per diem	$	$	$	$	$	$	$
	Operator Labor	Salary	$24,511	$2,200	$14,362	$16,519	$49,631	$	$107,223
		Travel	$	$	$	$	$	$	$
		Per diem	$	$	$	$	$	$	$
	Training	OSHA	$	$	$	$	$	$	$
		Procedures	$	$	$	$	$	$	$
	Maintenance	Concrete drill	$	$	$	$	$	$	$
	Consumables	Drop-Ex & Expray kits	$	$832	$	$	$	$	$832
		Personal protective equipment	$	$	$	$	$	$	$
		Laboratory supplies	$	$750	$2,500	$3,500	$4,766	$	$11,516
		Fuel	$	$	$	$	$	$	$
		Tools	$	$	$	$	$	$	$
		Other (Specified):	$	$	$	$	$	$	$
	Residual Waste Handling	N/A	$	$	$	$	$	$	$
	Off-site Disposal	Hazardous waste	$	$	$	$	$	$	$
	Analytical Laboratory Costs	NG – Method 8330/8332	$	$	$	$	$	$12,000	$12,000
		NC – MCAWW 353.2	$	$	$	$	$	$8,160	$8,160
		Shipping Costs	$	$	$	$	$	$300	$300
		Data validation	$	$	$	$	$	$2,370	$2,370
	Long Term Monitoring	N/A	$	$	$	$	$	$	$
Indirect Costs	Equipment Repair	Other (specified)	$	$	$	$	$	$	$
Demobilization	Housekeeping	Site cleanup/maintenance	$	$	$	$	$	$	$
		Personnel travel from site	$	$	$	$	$	$	$
		Equipment travel from site	$	$	$	$	$	$	$
		Shipping costs	$	$	$	$	$	$	$
		Total	$37,229	$10,493	$24,078	$27,237	$54,397	$22,830	$176,264

6.0 IMPLEMENTATION ISSUES

6.1 Environmental Checklist

There are no regulations envisioned that apply to the application of the field analytical methods for NC and NG determination.

6.2 Other Regulatory Issues

The primary regulatory/guidance issues that need to be resolved for the use of the field method technologies are the detection and quantitation limits as well as the data quality objectives, i.e., accuracy and precision requirements for the methods. The requirements need to be compared to the method capabilities to determine suitability.

6.3 End-User Issues

6.3.1 EXPRAY™ / DROPEX^{Plus} Test Kits for NC and NG

Overall EXPRAY™ and DROPEX^{Plus} are thought to be useful tools for screening the presence of significant concentrations of NC and or NG (0.1 to 1 percent and above) in the field or on sample extracts. Given its relatively low rate of false negative results, in combination with other field methods it could be a beneficial screening tool for identifying areas that contain explosive contamination in buildings above specified limits. Detectable levels are matrix dependent, with low confidence in results at or near the detection limit. The field method should only be used as a screening tool in combination with other supportive methods of analysis.

The EXPRAY™ / DROPEX^{Plus} tests (test kits) are inexpensive and easy to use. The EXPRAY™ test kit for 100 samples was $230 or $2.30 per sample and the DROPEX^{Plus} test kit for 50 samples was $186 or $3.72 per sample.

The EXPRAY™ test, while slightly less sensitive, was easier to evaluate as either detect or non-detect. DROPEX^{Plus} reagents seemed to spread out more on the test paper and had more prevalent yellow discoloration, which may interfere with detecting the positive pink color for the test.

Both of the field kits are easy to use with little specialized training and equipment except for analysis of sample extracts. Kits are designed for wipe tests of matrices using the supplied wipe papers, which can be completed in a matter of a few minutes. As tested however for analysis of the bulk matrices, the samples required crushing, homogenization and extraction prior to analysis, which complicates sample analysis and turns it into a lab procedure requiring more equipment and chemicals, analyst experience and significantly more time. Analysis times for extracted matrices will be about two hours due to the 1.5 hour solvent extraction time, as compared to a few minutes for the matrix surface wipe test.

6.3.2 CRREL Methodology for NC/NG

The CRREL RDX method of analysis gives a relatively low response for NC compared to NG that is easily impacted by matrix interferences. The wood matrix interfered with the method such that calibration with wood matrix standards could not be performed due to extremely low and non-reproducible response. The Modified CRREL method that was developed appears to

perform well for NC and NG analysis providing low detection limits in the range of 2 mg/kg to 10 mg/kg and predictable response for the matrices used in this test.

The analysis of NC and NG on concrete is hampered by decomposition of the explosive compounds by the concrete matrix due to its alkaline nature, which causes alkaline hydrolysis of the nitro groups. The instability of NC/NG compounds on concrete matrix makes analysis difficult not only due to the potential impact on samples during handling and preparation, but also due to the effect on matrix standards.

CRREL results are biased low in comparison to the STL reference method results. STL Method 353.2 results are believed to be biased high due to matrix interference or contamination phenomenon that was observed on method blanks and clean background matrix analyses.

Non-homogeneous sample material and sources of contamination, such as pieces of propellant material, make preparing a homogeneous sample difficult for reproducible results or split sample result comparison.

The CRREL method requires a small spectrophotometer in the $1,000 to $2,000 price range and assorted expendable supplies such as; reagents, syringes, sorbent tube cartridges and syringe filters. One field chemist with experience in wet chemistry techniques is required for onsite analysis by the modified CRREL method. Approximately 10 to 20 samples may be analyzed in a day depending on the amount of sample preparation required.

6.3.3 GC/TID Method for NG

GC/TID analysis of NG is selective and sensitive with detection limits in the range of 2 mg/kg to 5 mg/kg, which is comparable to the reference method. In general, reliability of the GC/TID ability to detect NG on the building materials is consistent with the reference Method 8330. Both methods may be subject to matrix interference effects and QC samples should be included to help assess data quality.

The GC/TID method requires a portable field GC with a TID, which is the most costly piece of equipment for use with these methods. The price for a portable GC/TID instrument is approximately $10,000. One field chemist with experience in gas chromatography is required for onsite analysis by GC/TID and it is estimated that 10 to 20 samples may be analyzed in a day depending on the sample matrix and the amount of sample preparation required.

Maintaining instrument sensitivity requires frequent cutting of the injection end of the column. The frequency is matrix dependent and thought to be due to loading or degradation of the column material by non-target constituents in the sample. This problem was most prevalent with the wood samples.

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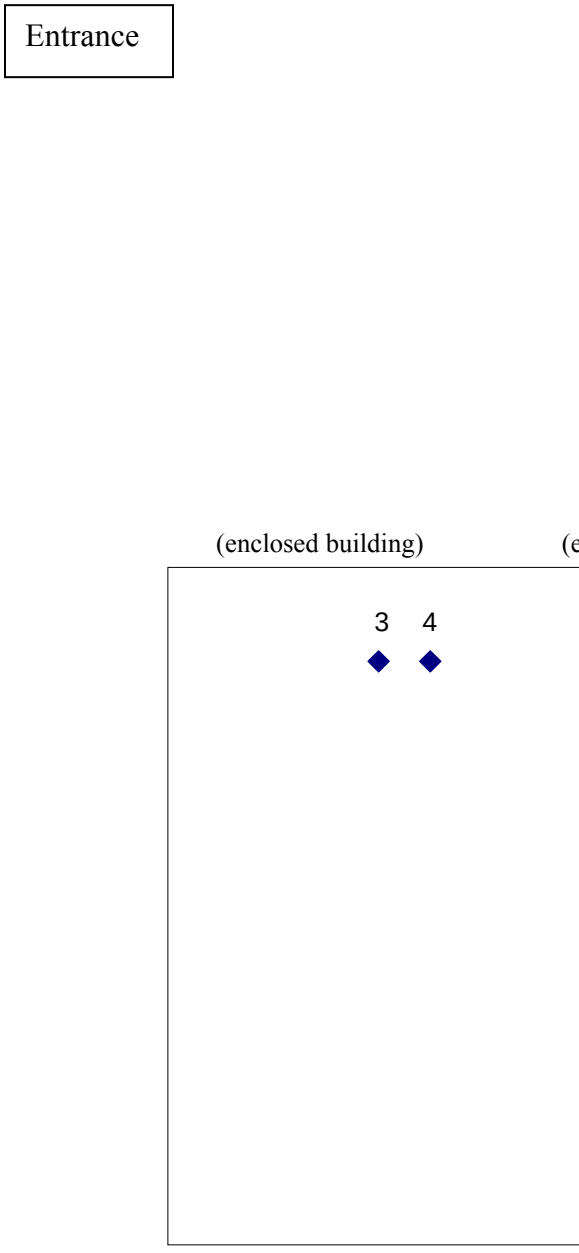
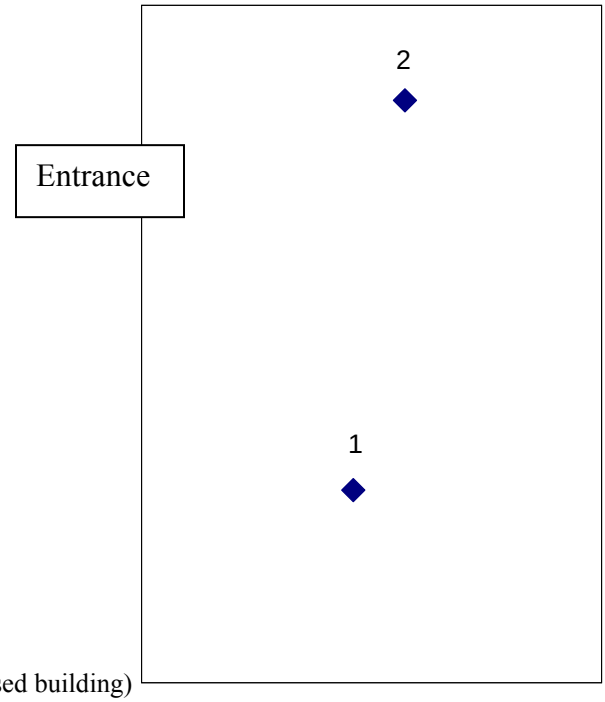
APPENDIX B.1
Sampling Building Maps

6657-02 Neutralizer House

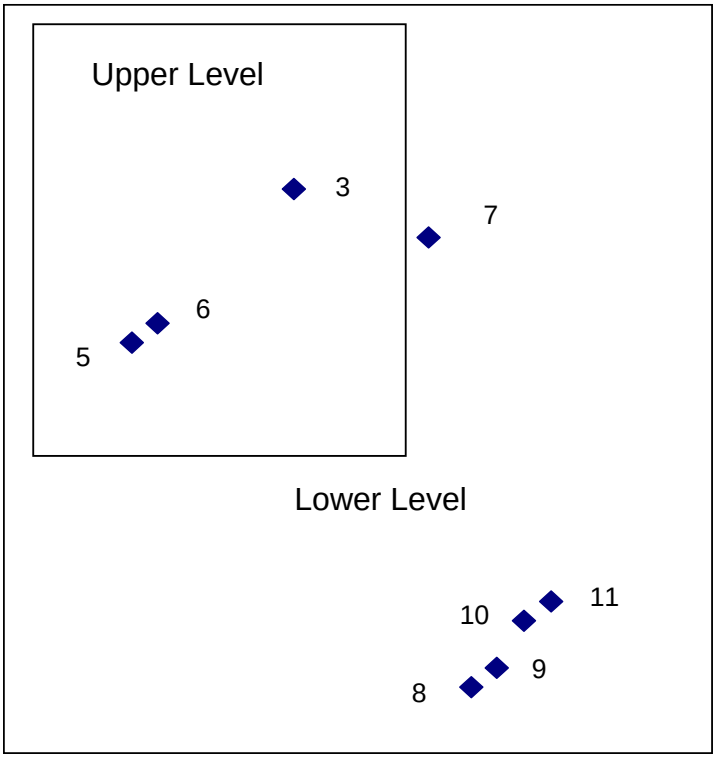


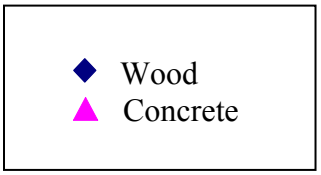
6657-02 Nitrate House



Bldg. 5024 Boiling Tub House

(enclosed building - large 2-story warehouse)

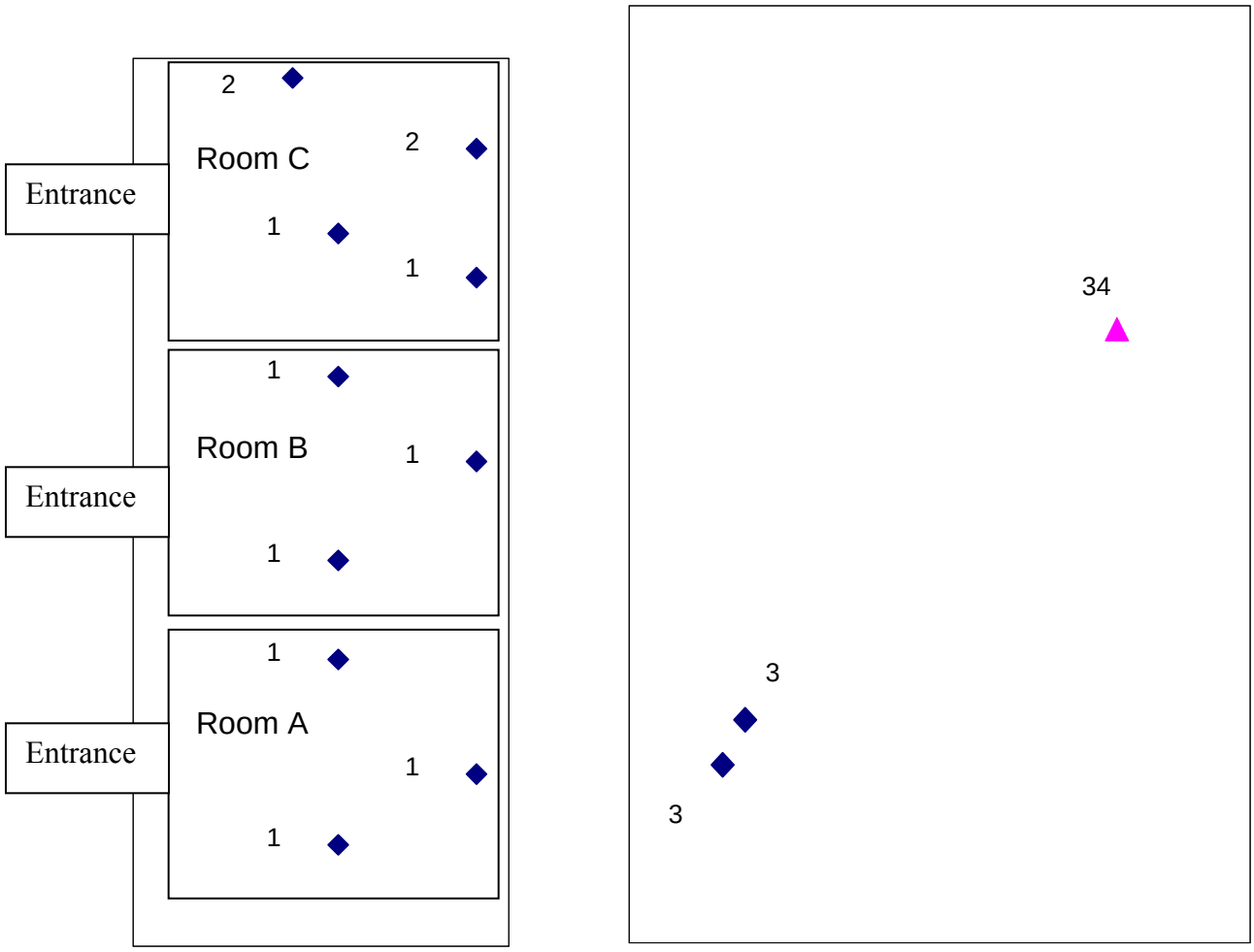


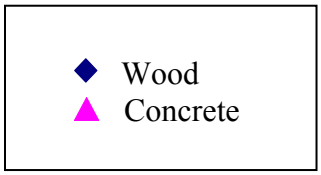


Southwest Entrance

Bldg. 6709-17 Pre-Drying House
(enclosed building)

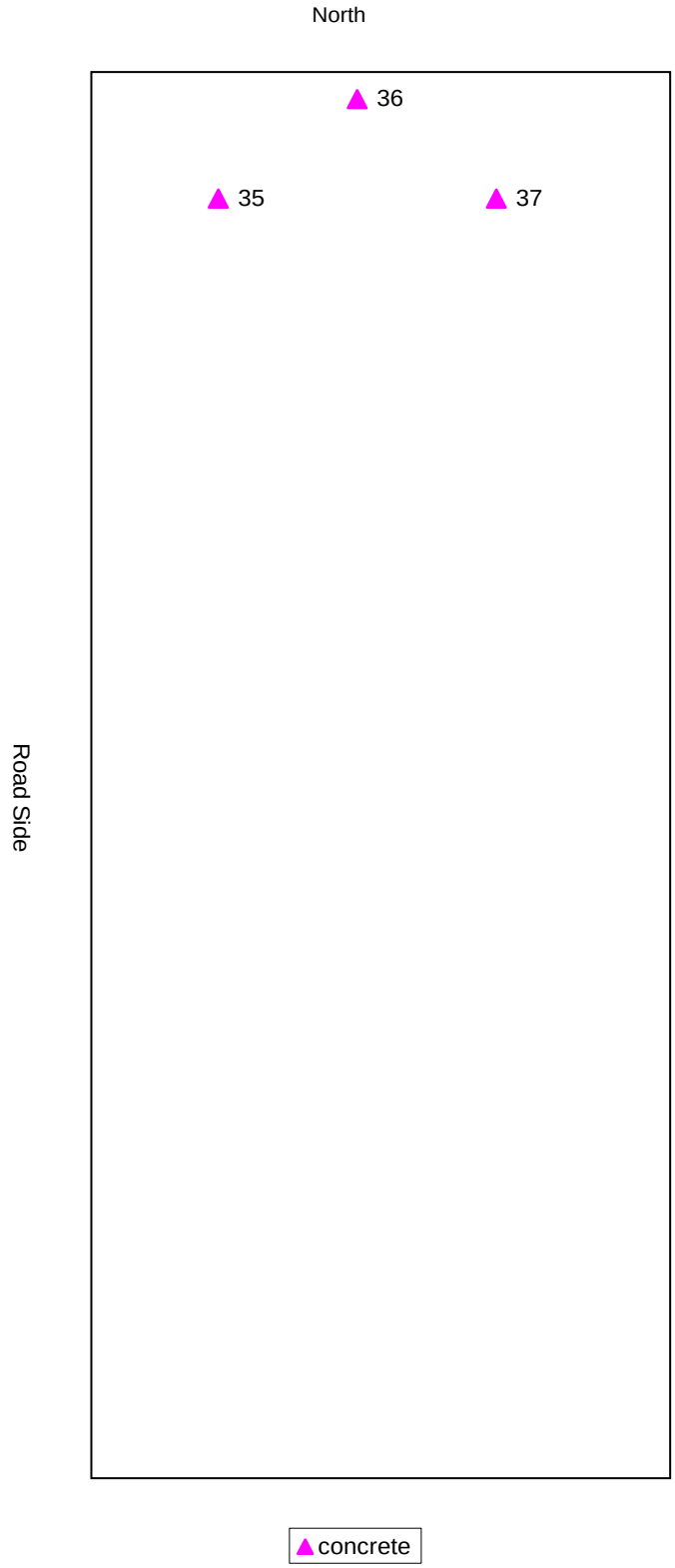
Bldg. 9590 Powder Storage Pit
(enclosed building – large pit warehouse)





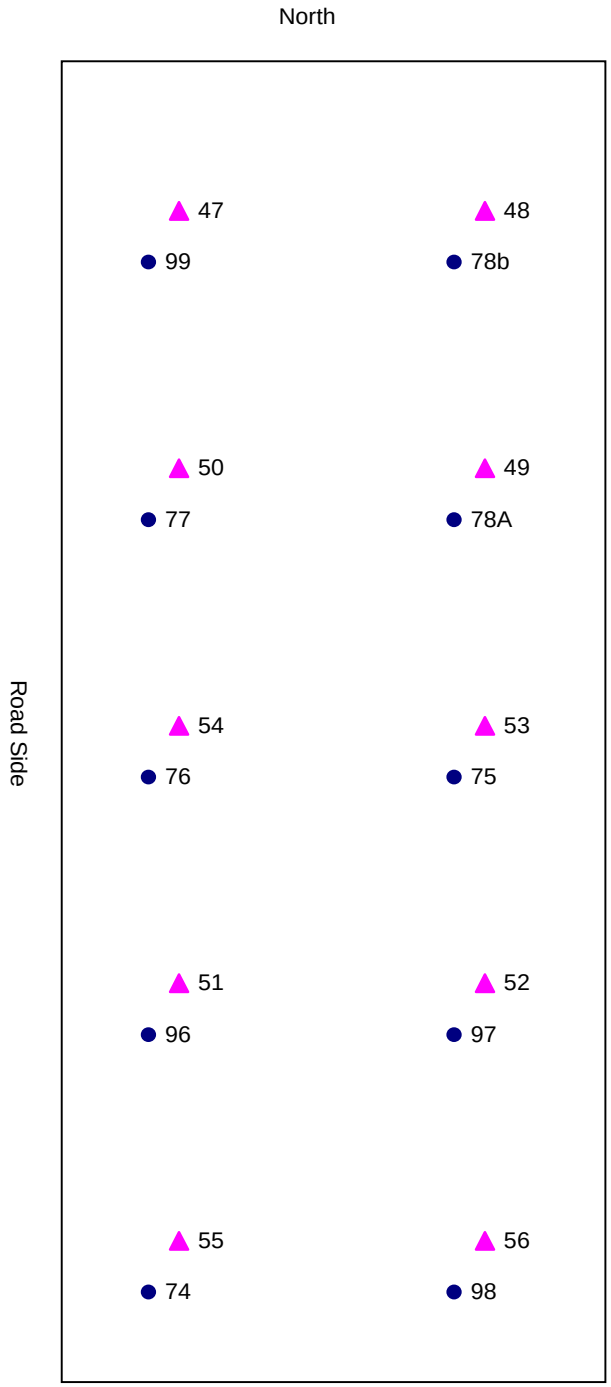
Bldg. 1885-01 Box Storage House

(enclosed building – large empty warehouse)



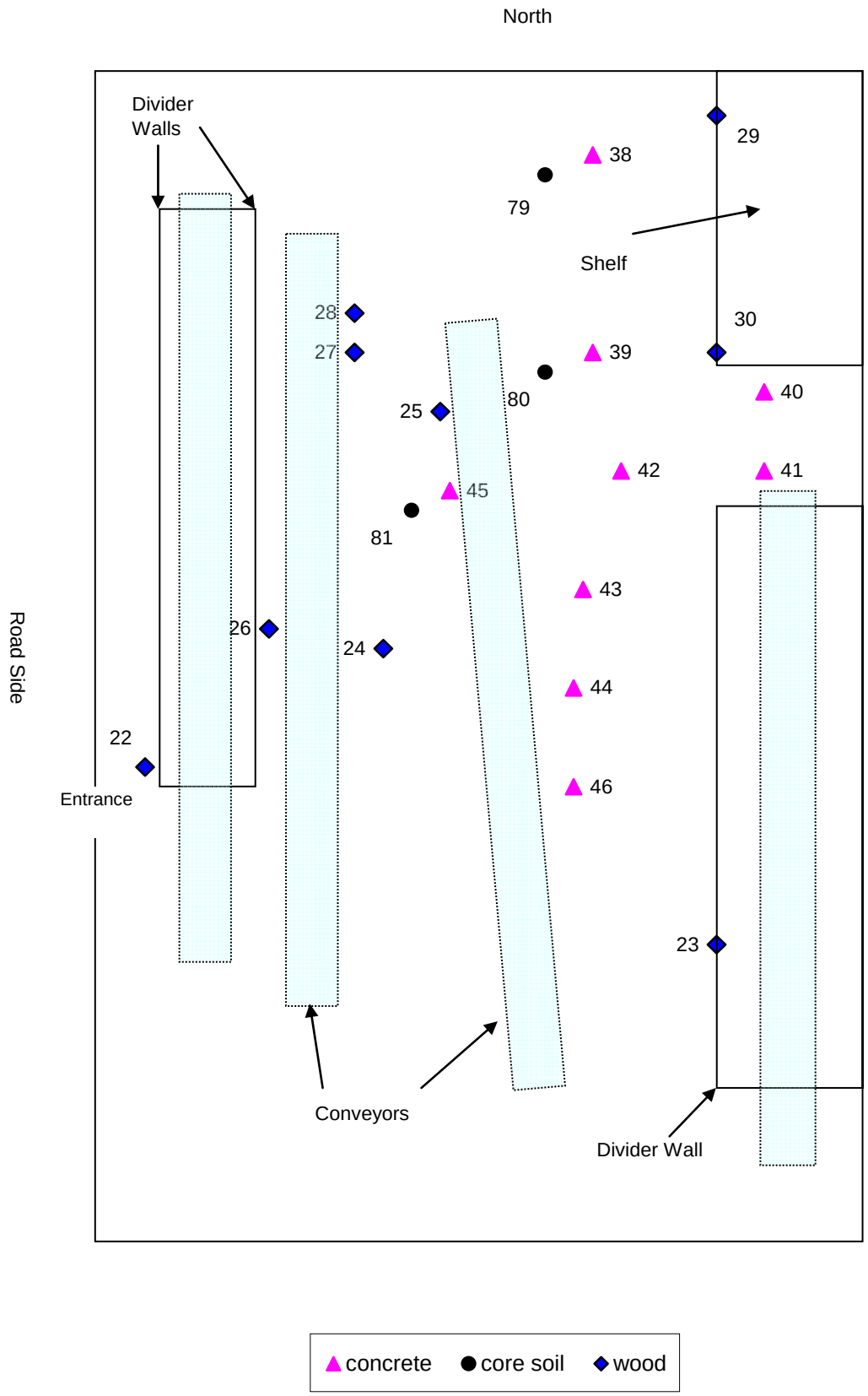
Bldg. 1885-02 Box Storage House (open concrete slab)

Bldg. 1885-03 Box Storage House (open concrete slab)



Note: Soil sample 78 is composite of 78a +78b

Bldg. 1890-01 Box Wash House (enclosed building)



APPENDIX B.2
Lab Data Summary Tables

Table B.2-1 BAAAP/ESTCP Field Demonstration Wood Analytical Summary

Sample Identification	Matrix	QC Spike Description mg/K	Sampl wt (g)	Aceton ml	STL Reference Method Results (mg/kg)				Drop-Ex	Expray	NG GC/TID	Shaw Modified NG+NC				Comments/ Notes		
					Metho 8330 NG	Metho 353.2 NC	Corr. Metho 353.2 NC	Corr. Total NG+NC	Extrac (10 uls)	Extrac (10 uls)	NG Conc mg/K	Abs 507n Reading 1	Analysis Dilution Factor	Analyzed conc as NG	Analyzed conc as NC			
BI-BLK-001-WD-NG	Wood	N	20	60	N	N	N	N	-	-	ND<5.0	0.003	1	ND<5	ND<10			
BI-LCS-001-WD-NG	Wood	100	20	60	N	N	N	N	+	-	102	0.824	1	110	N			
BI-LCS-001-WD-NC	Wood	211	N	N	N	N	N	N	+	+	N	1.286	1	N	231			
6657-02N-WD-001	Wood	N	20	60	3.7J	190J	377	381	-	-	ND<5.0	0.025	1	5	13			
6657-02N-WD-002	Wood	N	20	60	18	851Q,J	1690	1710	-	-	3.22 J	0.180	1	25	40			
6657-02I-WD-003	Wood	N	20	60	ND<0.5	39.9J	79	79	-	-	ND<5.0	0.008	1	ND<5	ND<10			
6657-02I-WD-003A	Wood	N	20	60	ND<5	43.2J	86	86	-	-	ND<5.0	0.005	1	ND<5	ND<10			
6657-02I-WD-004	Wood	N	20	60	ND<0.5	1020Q,J	2020	2020	-	-	ND<5.0	0.021	1	4	13			
5024-000-WD-005	Wood	N	20	60	ND<5	221J	438	438	+	-	7.67	0.382	3.33	172	250			
5024-000-WD-006	Wood	N	20	60	ND<5	174J	345	345	+	-	ND<5.0	0.267	3.33	122	184			
5024-000-WD-007	Wood	N	20	60	ND<5	697Q,J	1380	1380	+	-	ND<5.0	0.350	3.33	158	231			
5024-000-WD-008	Wood	N	20	60	ND<5	40.5J	80	80	-	-	ND<5.0	0.065	1	10	20			
5024-000-WD-009	Wood	N	20	60	ND<0.5	44.6J	88	88	-	-	ND<5.0	0.058	1	9	19			
5024-000-WD-010	Wood	N	20	60	ND<5	332J	659	659	++	++	ND<5.0	0.648	6.67	579	806			
5024-000-WD-011	Wood	N	20	60	ND<2.5	138J	274	274	+	+	ND<5.0	0.422	1.67	95	137			
6709-17-WD-012	Wood	N	20	60	99	143J	284	383	+	-	31.6	0.104	6.67	101	180			
6709-17-WD-013	Wood	N	20	60	88	115J	228	316	+	-	19.2	0.059	6.67	62	129			
6709-17-WD-014	Wood	N	20	60	230	198J	393	623	+	+	98.3	0.492	6.67	442	627			
6709-17-WD-015	Wood	N	20	60	240	198J	393	633	+	++	104	0.742	6.67	661	914			
6709-17-WD-016	Wood	N	20	60	180	156J	310	490	+	-	47.3	0.079	6.67	79	152			
6709-17-WD-017	Wood	N	20	60	130	172J	341	471	+	-	44.5	0.110	6.67	106	187			
6709-17-WD-018	Wood	N	20	60	84	122J	242	326	+	-	22.9	0.044	6.67	49	111			
6709-17-WD-019	Wood	N	20	60	120	149J	296	416	+	-	44.5	0.084	6.67	84	157			
6709-17-WD-019MS-NG	Wood	200	10	30	N	N	N	N	+	+	217	0.608	6.67	544	N			
6709-17-WD-019MSD-NG	Wood	200	10	30	N	N	N	N	+	+	238	0.701	6.67	625	N			
6709-17-WD-019MS-NC	Wood	421	10	30	N	N	N	N	+	+	N	0.617	6.67	N	770			
6709-17-WD-019MSD-NC	Wood	421	10	30	N	N	N	N	+	+	N	0.625	6.67	N	779			
6709-17-WD-020	Wood	N	20	60	110	96.2J	191	301	+	-	25.4	0.091	6.67	90	165			
6709-17-WD-020A	Wood	N	20	60	120	113J	224	344	+	-	25.9	0.125	6.67	120	204			
BI-BLK-002-WD-NG	Wood	N	20	60	N	N	N	N	-	-	ND<5.0	0.001	1	ND<5	ND<10			
BI-LCS-002-WD-NG	Wood	50	20	60	N	N	N	N	+	-	46.1	0.158	2	45	N			
BI-LCS-002-WD-NC	Wood	211	20	60	N	N	N	N	+	+	ND<5.0	0.428	3.33	N	187			
BI-BLK-003-WD-NG	Wood	N	20	60	N	N	N	N	-	-	ND<5.0	0.000	1	ND<5	ND<10			
BI-LCS-003-WD-NG	Wood	200	20	60	N	N	N	N	+	-	161	0.511	4	276	391			
BI-LCS-003-WD-NC	Wood	211	20	60	N	N	N	N	+	+	N	0.241	3.33	112	170			

Table B.2-1 BAAAP/ESTCP Field Demonstration WoodAnalytical Summary Cont.

Sample Identification	Matrix	QC Sample Spike Description mg/Kg	Sample wt (g)	Acetone mls	STL Reference Method Results (mg/kg)				Drop-Ex	Expray	NG GC/TID	Shaw Modified CRREL NG+NC				Comments/ Notes
					Method 8330 NG	Method 353.2 NC	Corr. Method 353.2 NC	Corr. Total NG+NC	Extract (10 uls)	Extract (10 uls)	NG Conc mg/Kg	Abs at 507nm Reading 1	Analysis Dilution Factor	Analyzed conc as NG	Analyzed conc as NC	
6709-17-WD-021	Wood	NA	20	60	62	286JB	567	629	++	++	58.5	0.504	10	682	965	
1890-01-WD-022	Wood	NA	20	60	ND<0.5	35.3JB	70	70	+-	-	ND<5.0	0.006	1	ND<5	ND<10	
1890-01-WD-022MS-NG	Wood	100	10	30	NA	NA	NA	NA	+	+-	101	0.064	10	103	NA	
1890-01-WD-022MSD-NG	Wood	100	10	30	NA	NA	NA	NA	+	+-	84.8	0.063	10	102	NA	
1890-01-WD-022MS-NC	Wood	211	10	30	NA	NA	NA	NA	+	+	NA	0.329	3.33	NA	221	
1890-01-WD-022MSD-NC	Wood	211	10	30	NA	NA	NA	NA	+	+	NA	0.358	3.33	NA	238	
1890-01-WD-023	Wood	NA	20	60	ND<0.5	19.1JB	38	38	-	-	ND<5.0	0.000	1	ND<5	ND<10	
1890-01-WD-024	Wood	NA	20	60	ND<0.5	27.6JB	55	55	-	-	ND<5.0	0.000	1	ND<5	ND<10	
1890-01-WD-025	Wood	NA	20	60	ND<0.5	61.8JB	123	123	+-	-	ND<5.0	0.032	1	6	15	
1890-01-WD-026	Wood	NA	20	60	ND<0.5	19.8JB	39	39	-	-	ND<5.0	0.000	1	ND<5	ND<10	
1890-01-WD-027	Wood	NA	20	60	ND<5	46.3JB	92	92	+	-	ND<50	0.135	1	20	33	
1890-01-WD-028	Wood	NA	20	60	ND<5	29.1JB	58	58	-	-	ND<5.0	0.147	1	21	35	
1890-01-WD-028A	Wood	NA	20	60	ND<5	42.4JB	84	84	-	-	ND<5.0	0.158	1	23	37	
1890-01-WD-029	Wood	NA	20	60	ND<5	56.5JB	112	112	-	-	ND<5.0	0.170	1	24	39	
1890-01-WD-030	Wood	NA	20	60	ND<5	46.6JB	92	92	+-	-	ND<5.0	0.252	1	35	53	
9590-000-WD-031	Wood	NA	20	60	ND<0.5	42.9JB	85	85	+	-	ND<5.0	0.636	3.33	285	397	
9590-000-WD-032	Wood	NA	20	60	ND<10	54.8JB	109	109	-	-	ND<50	0.000	1	ND<5	ND<10	
5024-000-WD-033	Wood	NA	20	60	ND<0.5	2880Q,JB	5710	5710	+++	+++	ND<20	0.194	66.6	1830	2870	
5024-000-WD-033A	Wood	NA	20	60	ND<0.5	7080Q,JB	14000	14000	+++	+++	ND<20	0.190	66.6	1790	2820	

Q= Elevated reporting Limit

J = Estimated result. Result is less than reporting limits.

JS = Estimated result. Surrogate recovery is outside stated control limits and reanalysis was outside hold time.

JB = Estimated result. Method blank contains contamination.

PG = The percent difference between the original and confirmation analysis is greater than 40%.

ND = Not detected at the specified method detrection limit

NA = Not analyzed or not applicable

+ = Detected

- = Not detected

+- = Possible detection; slight coloration, but difference from blank color was inconclusive

Table B.2-2 BAAAP/ESTCP Field Demonstration Soil Analytical Summary

					STL Reference Method Results				Drop-Ex	Expra	GC/TID NG	CRRE NG+N			Shaw Modified CRREL NG+N			
Sample Identification	Matri	QC Sample Spik Descriptio mg/K	Sample (g)	Acetone mls	Method 8330 NG	Method 353.2 N	Corr. Method 353.2 N	Corr. Total NG+N	Extract (10	Extract (10	NG Conc mg/K	Abs 507nm	Analysis Dilution Factor	Conc N mg/k	Abs 507nm	Analysis Dilution Factor	Conc as mg/k	Comments/
BI-BLK-001-SS-NG	Soi	N	20	20	N	N	N	N	-	-	ND<2.0	0.007	1	ND<25	0.000	2.3	ND<4	
BI-LCS-001-SS-NG	Soi	50	20	20	N	N	N	N	+	+	45.6	0.406	10	56.1	0.294	10	54	*calculated as
BI-LCS-001-SS-NC	Soi	200	20	20	N	N	N	N	+	+	N	0.275	1	255	0.306	25	163	
1885-02-SS-067	Soi	N	20	20	ND<0.5	203Q	314	314	+	+	ND<2.0	0.021	1	ND<25	0.041	38	ND<57	no more sample
1885-02-SS-068	Soi	N	20	20	0.55	551Q	852	853	++	++	ND<2.0	0.276	1	256	0.236	76	382	
1885-02-SS-069	Soi	N	20	20	0.36J,J	400Q	619	619	++	+	ND<2.0	0.015	2	ND<50	0.117	36.4	91	
1885-02-SS-070	Soi	N	20	20	ND<0.5	57.6	89	89	++	+	ND<2.0	0.094	1	82.9	NS	NS	NS	no more sample
1885-02-SS-071	Soi	N	20	20	ND<0.5	11.2	17	17	-	-	ND<2.0	0.000	1	ND<25	0.031	2.9	ND<5	
1885-02-SS-071MS NG	Soi	37.5	20	20	N	N	N	N	+	-	39.1	0.292	10	40.9	0.367	10	67	*calculated as
1885-02-SS-071MSD NG	Soi	37.5	20	20	N	N	N	N	+	-	39.5	0.256	10	36.1	0.413	10	75	*calculated as
1885-02-SS-071MS NC	Soi	37.5	20	20	N	N	N	N	+	-	N	0.00	1	ND<25	0.020	25	ND<38	no more sample
1885-02-SS-071MSD NC	Soi	37.5	20	20	N	N	N	N	+	-	N	0.00	1	ND<25	0.016	25	ND<38	no more sample
1885-02-SS-072[a]	Soi	N	20	20	2.1J	6200Q	9590	9590	+++	++	22.0	0.457	10	4290	0.710	500	7570	GC/TID extract, no resin
1885-02-SS-072A[a]	Soi	N	20	20	1.4PG,JS	6640Q	10300	10300	++++	+++	44.5	0.795	10	7500	0.808	500	8610	GC/TID extract, no resin
1885-02-SS-073[b]	Soi	N	20	20	ND<0.5	11.8	18	18	+	-	ND<2.0	0.091	1	80.0	0.495	3.2	34	
1885-03-SS-074	Soi	N	20	20	ND<0.5	2.5	4	4	-	-	ND<2.0	0.005	1	ND<25	0.000	1.8	ND<3	
1885-03-SS-075	Soi	N	20	20	ND<0.5	39.6	61	61	-	-	ND<2.0	0.046	1	37.1	0.002	4.4	ND<7	
1885-03-SS-076	Soi	N	20	20	ND<0.5	51.3	79	79	+	-	ND<2.0	0.019	1	ND<25	0.116	5	12	
1885-03-SS-077	Soi	N	20	20	ND<0.5	15.0	23	23	-	-	ND<2.0	0.000	1	ND<25	0.007	2.4	ND<4	
1885-03-SS-078	Soi	N	20	20	ND<0.5	31.4	49	49	-	-	ND<2.0	0.000	1	ND<25	0.063	3.2	ND<5	
1890-01B-SS-079	Soi	N	20	20	ND<0.5	3.2	5	5	-	-	ND<2.0	0.000	1	ND<25	0.000	1.7	ND<3	
1890-01B-SS-080	Soi	N	20	20	0.55J	182Q	282	282	+	+	3.0	0.201	1	185	0.461	15	147	
1890-01B-SS-081	Soi	N	20	20	ND<0.5	11.6	18	18	+	+	ND<2.0	0.005	1	ND<25	0.984	2	42	
1890-01B-SS-081A	Soi	N	20	20	ND<0.5	39.5	61	61	-	-	ND<2.0	0.001	1	ND<25	0.004	4.0	ND<6	
1890-01B-SS-081B	Soi	N	20	20	N	N	N	N	N	N	N	N	N	N	0.000	3	ND<5	
1890-01B-SS-081C	Soi	N	20	20	N	N	N	N	N	N	N	N	N	N	0.000	3	ND<5	
BI-BLK-002-SS-NC/NG	Soi	N	20	20	N	N	N	N	-	-	ND<2.0	0.000	1	ND<25	0.000	1	ND<2	
BI-LCS-002-SS-NG	Soi	50	20	20	N	N	N	N	-	-	55.0	0.359	10	50.8	0.275	15.4	78	*calculated as
BI-LCS-002-SS-NC	Soi	200	20	20	N	N	N	N	+	+	N	0.177	1	169	NS	NS	NS	no more sample
1885-02-SS-082	Soi	N	20	20	1.0	1970Q, JB	3050	3050	+	++	ND<2.0	0.072	1	68.6	0.550	20	235	GC/TID extract, SPICE column

Table B.2-2 BAAAP/ESTCP Field Demonstration Soil Analytical Summary Cont.

					STL Reference Method Results (mg/kg)				Drop-Ex	Expray	GC/TID NG	CRREL NG+NC			Shaw Modified CRREL NG+NC			
1885-02-SS-083	Soil	NA	20	20	3.0JS	275Q,JB	425	428	+	++	ND<2.0	0.047	1	44.8	0.509	15	163	GC/TID extract, SPICE column
1885-02-SS-083A	Soil	NA	20	20	ND<0.5JS	431Q,JB	667	667	+	+	ND<2.0	0.021	1	ND<25	0.214	40	183	
1885-02-SS-084	Soil	NA	20	20	ND<0.5	234Q,JB	362	362	+	+	ND<2.0	0.060	1	57.1	0.520	21	233	
1885-02-SS-085	Soil	NA	20	20	0.19J	174Q,JB	269	269	+	+	ND<2.0	0.032	1	30.5	0.398	15	127	
1885-02-SS-086	Soil	NA	20	20	ND<0.5	21.4JB	33	33	-+	-	ND<2.0	0.016	1	ND<25	0.533	1.5	17	GC/TID extract, SPICE column
1885-02-SS-087	Soil	NA	20	20	0.82	558Q,JB	863	864	+	+	ND<2.0	0.056	1	53.3	0.210	56	251	
1885-02-SS-087MS NG	Soil	50	20	20	NA	NA	NA	NA	+	+	55.5	0.226	10	33.1	0.864	10	184	
1885-02-SS-087MSD NG	Soil	50	20	20	NA	NA	NA	NA	+	+	54.8	0.235	10	34.3	0.542	50	578	
1885-02-SS-087MS NC	Soil	316	20	20	NA	NA	NA	NA	+	+	NA	0.067	1	63.8	0.527	25	281	
1885-02-SS-087MSD NC	Soil	316	20	20	NA	NA	NA	NA	+	+	NA	0.090	1	85.7	0.365	25	195	
1885-02-SS-088	Soil	NA	20	20	0.39J	11.2JB	17	18	-	-	ND<2.0	0.000	1	ND<25	0.000	3	ND<5	
1885-02-SS-089	Soil	NA	20	20	ND<0.5	24.4JB	38	38	-	-	ND<2.0	0.000	1	ND<25	0.109	3	7	
1885-02-SS-090	Soil	NA	20	20	ND<0.5	2.8J, JB	4	4	-	-	ND<2.0	0.001	1	ND<25	0.000	2	ND<3	
1885-02-SS-091	Soil	NA	20	20	ND<0.5	266Q,JB	412	412	+	+	ND<2.0	0.044	1	41.9	0.393	100	838	
1885-02-SS-092	Soil	NA	20	20	ND<0.5	37.4JB	58	58	+	-+	ND<2.0	0.006	1	ND<25	0.273	4	23	
1885-02-SS-093	Soil	NA	20	20	0.18J	340Q,JB	526	526	-	-	ND<2.0	0.005	1	ND<25	0.010	30	ND<45	
1885-02-SS-093A	Soil	NA	20	20	ND<0.5	92.2Q,JB	143	143	-	-	ND<2.0	0.003	1	ND<25	0.001	9	ND<15	no more sample
1885-02-SS-094	Soil	NA	20	20	ND<0.5	9.9JB	15	15	-	-	ND<2.0	0.006	1	ND<25	0.000	2.3	ND<4	
1885-02-SS-095	Soil	NA	20	20	ND<0.5	66.8JB	103	103	-+	+	ND<2.0	0.016	1	ND<25	0.700	7	104	
1885-02-SS-096	Soil	NA	20	20	ND<0.5	2.3J,JB	4	4	-	-	ND<2.0	0.001	1	ND<25	NS	NS	NS	no more sample
1885-02-SS-097	Soil	NA	20	20	ND<0.5	87.9Q,JB	136	136	+-	-	ND<2.0	0.003	1	ND<25	0.053	8	9	
1885-02-SS-098	Soil	NA	20	20	ND<0.5	55.7JB	86	86	++	+	ND<2.0	0.011	1	ND<25	NS	NS	NS	no more sample
1885-02-SS-099	Soil	NA	20	20	ND<0.5	62.5JB	97	97	+	+-	ND<2.0	IF	1	NA	0.105	5	11	

[a]Solid propellant pieces (0.023 g) were physically removed from 695 g of soil during sample preparation (33.1 mg/kg).

[b]Solid propellant pieces (0.56 g) were physically removed from 445 g of soil during sample preparation (1,260 mg/kg).

Q= Elevated reporting Limit

J = Estimated result. Result is less than reporting limits.

JS = Estimated result. Surrogate recovery is outside stated control limits and reanalysis was outside hold time.

JB = Estimated result. Method blank contains contamination.

PG = The percent difference between the original and confirmation analysis is greater than 40%.

ND = Not detected at the specified method detection limit

NA = Not analyzed or not applicable

+ = Detected

- = Not detected

+- = Possible detection; slight coloration, but difference from blank color was inconclusive

Table B.2-3 BAAAP/ESTCP Field Demonstration Concrete Material Analytical Summary

					STL Reference Method Results				Core Surface Drop-Ex Test			Drop-Ex	Expra	NG GC/TID	CRREL NG+N				
Sample Identification	Matrix	QC Spike Description mg/K	Sampl wt (g)	Aceton ml	Method 8330 NG	Method 353.2 N	Corr. Method 353.2 N	Corr. Total NG+N	Top	Bottom	Crack	Extract (10	Extract (10	NG Conc mg/K	Abs 507nm Reading	Analysis Dilution Factor	Analyzed conc as NG	Analyzed conc as NG	Comments/
BI-BLK-001-CM-NG	Concrete	N	20.0	20.0	N	N	N	N	N	N	N	-	-	ND<2.0	0.000	1	ND<5.0	ND<100	
BI-LCS-001-CM-NG	Concrete	50	20.0	20.0	N	N	N	N	N	N	N	+	-	41	0.474	1	53.7	N	
BI-BLK-001-CM-NC	Concrete	N	20.0	20.0	N	N	N	N	N	N	N	-	-	N	0.000	1	ND<5.0	ND<100	
BI-LCS-001-CM-NC	Concrete	211	20.0	20.0	N	N	N	N	N	N	N	-	-	N	0.020	1	ND<5.0	ND<100	
9590-000-CM-034	Concrete	N	20.0	20.0	ND<0.5	201Q	413	413	++	-	-	-	-	ND<2.0	0.017	1	ND<5.0	ND<100	
9590-000-CM-034A	Concrete	N	20.0	20.0	ND<0.5	63.0	129	129	++	N	N	-	-	ND<2.0	0.007	1	ND<5.0	ND<100	
1885-01-CM-035	Concrete	N	20.0	20.0	ND<0.5	17.1	35	35	+	+	N	+-	-	ND<2.0	0.007	1	ND<5.0	ND<100	
1885-01-CM-035	Concrete	N	20.0	20.0	N	N	N	N	N	+	N	+-	-	ND<2.0	0.001	1	ND<5.0	ND<100	
1885-01-CM-036	Concrete	N	20.0	20.0	ND<0.5	20.3	42	42	+-	+-	N	-	-	ND<2.0	0.000	1	ND<5.0	ND<100	Wipe of EJM -
1885-01-CM-037	Concrete	N	20.0	20.0	ND<0.5	17.9	37	37	+	+	N	-	-	ND<2.0	0.006	1	ND<5.0	ND<100	
1890-01B-CM-038	Concrete	N	20.0	20.0	ND<0.5	5.7	12	12	-	-	N	-	-	ND<2.0	0.004	1	ND<5.0	ND<100	
1890-01B-CM-038MS-NC	Concrete	211	20.0	20.0	N	N	N	N	N	N	N	+	+-	ND<2.0	0.018	1	N	ND<100	
1890-01B-CM-038MSD-NC	Concrete	211	20.0	20.0	N	N	N	N	N	N	N	+	+-	ND<2.0	0.056	1	N	114	
1890-01B-CM-038MS-NG	Concrete	100	20.0	20.0	N	N	N	N	N	N	N	+	+	172	O	1	O	N	
1890-01B-CM-038MSD-NG	Concrete	100	20.0	20.0	N	N	N	N	N	N	N	+	+	156	O	1	O	N	
1890-01B-CM-039	Concrete	N	20.0	20.0	ND<0.5	30.1	62	62	+	+	N	-	-	ND<2.0	-0.002	1	ND<5.0	ND<100	
1890-01B-CM-040	Concrete	N	20.0	20.0	ND<0.5	17.8	37	37	+	+	N	-	-	ND<2.0	-0.005	1	ND<5.0	ND<100	
1890-01B-CM-041	Concrete	N	20.0	20.0	ND<0.5	9.9	20	20	+	+	N	-	-	ND<2.0	0.018	1	ND<5.0	ND<100	
1890-01B-CM-042	Concrete	N	20.0	20.0	ND<0.5	95.9Q	197	197	+	+	N	-	-	ND<2.0	0.008	1	ND<5.0	ND<100	
1890-01B-CM-043	Concrete	N	20.0	20.0	ND<0.5	71.9Q	148	148	++	+	++	-	-	ND<2.0	0.002	1	ND<5.0	ND<100	
1890-01B-CM-043A	Concrete	N	20.0	20.0	ND<0.5	36.8	76	76	N	N	N	-	-	ND<2.0	0.000	1	ND<5.0	ND<100	
1890-01B-CM-044	Concrete	N	20.0	20.0	ND<0.5	10.2	21	21	-	-	N	-	-	ND<2.0	0.000	1	ND<5.0	ND<100	
1890-01B-CM-045	Concrete	N	20.0	20.0	0.23	87.8Q	180	180	-	-	N	-	-	ND<2.0	0.000	1	ND<5.0	ND<100	
1890-01B-CM-046	Concrete	N	20.0	20.0	1.1	261Q	536	537	++	++	N	+	-	2.52	0.061	1	8.8	124	Wipe of EJM ++
1890-01B-CM-046A	Concrete	N	20.0	20.0	0.46	42.7	88	88	N	N	N	+	-	1.44	0.063	1	9.0	128	
1890-01B-CM-046(B)	Concrete	N	20.0	20.0	N	N	N	N	N	N	N	N	N	N	0.081	10	N	87	Shaw Modified CRREL
1890-01B-CM-046(C)	Concrete	N	20.0	20.0	N	N	N	N	N	N	N	N	N	N	0.297	10	N	230	Shaw Modified CRREL
1885-03S-CM-047	Concrete	N	20.0	20.0	ND<0.5	3.1J	6	6	-	-	-	-	-	ND<2.0	0.007	1	ND<5.0	ND<100	
1885-03S-CM-048	Concrete	N	20.0	20.0	ND<0.5	3.0J	6	6	-	-	N	-	-	ND<2.0	-0.003	1	ND<5.0	ND<100	
1885-03S-CM-049	Concrete	N	20.0	20.0	ND<0.5	6.8J	14	14	-	-	N	-	-	ND<2.0	0.006	1	ND<5.0	ND<100	Wipe of EJM -
1885-03S-CM-050	Concrete	N	20.0	20.0	ND<0.5	3.4J	7	7	-	-	N	-	-	ND<2.0	0.001	1	ND<5.0	ND<100	Wipe of EJM -
BI-BLK-002-CM-NG	Concrete	N	20.0	20.0	N	N	N	N	N	N	N	-	-	ND<2.0	-0.001	1	ND<5.0	ND<100	
BI-LCS-002-CM-NG	Concrete	50	20.0	20.0	N	N	N	N	N	N	N	-	-	48.2	0.396	1	45.2	N	
BI-BLK-002-CM-NC	Concrete	N	20.0	20.0	N	N	N	N	N	N	N	-	-	N	0.003	1	ND<5.0	ND<100	
BI-LCS-002-CM-NC	Concrete	211	20.0	20.0	N	N	N	N	N	N	N	-	-	N	0.018	1	ND<5.0	ND<100	
1885-03-CM-051	Concrete	N	20.0	20.0	ND<0.5	3.2J	7	7	-	-	N	-	-	ND<2.0	0.025	1	ND<5.0	ND<100	
1885-03-CM-052	Concrete	N	20.0	20.0	ND<0.5	5.3J	11	11	-	-	N	-	-	ND<2.0	0.003	1	ND<5.0	ND<100	
1885-03-CM-053	Concrete	N	20.0	20.0	ND<0.5	8.8J	18	18	-	-	N	-	-	ND<2.0	0.005	1	ND<5.0	ND<100	

Table B.2-3 BAAAP/ESTCP Field Demonstration Concrete Material Analytical Summary Cont.

Sample Identification	Matrix	QC Sample Spike Description mg/Kg	Sample wt (g)	Acetone mls	STL Reference Method Results (mg/kg)				Core Surface Wipes Drop-Ex Test			Drop-Ex	Expray	NG GC/TID	CRREL NG+NC				Comments/ Notes
					Method 8330 NG	Method 353.2 NC	Corr. Method 353.2 NC	Corr. Total NG+NC	To	Botto	Crack	Extract (10 uls)	Extract (10 uls)	NG Conc mg/Kg	Abs at 507nm Reading 1	Analysis Dilution Factor	Analyzed conc as NG	Analyzed conc as NC	
1885-03-CM-054	Concrete	NA	20.0	20.0	ND<0.5	5.0JM	10	10	-	-	N	-	-	ND<2.0	0.006	1	ND<5.0	ND<100	
1885-03-CM-055	Concrete	NA	20.0	20.0	ND<0.5	4.0JM	8	8	N	N	N	-	-	ND<2.0	0.022	1	ND<5.0	ND<100	
1885-03-CM-056	Concrete	NA	20.0	20.0	ND<0.5	9.8JM	20	20	+-	N	+-	-	-	ND<2.0	0.007	1	ND<5.0	ND<100	Fractured vertical
1885-02-CM-057	Concrete	NA	20.0	20.0	ND<0.5	36.1JM	74	74	-	-	N	-	-	ND<2.0	0.002	1	ND<5.0	ND<100	
1885-02-CM-058	Concrete	NA	20.0	20.0	ND<0.5	3.1JM	6	6	-	N	N	-	-	ND<2.0	0.002	1	ND<5.0	ND<100	
1885-02-CM-059	Concrete	NA	20.0	20.0	ND<0.5	6.1JM	13	13	-	-	N	-	-	ND<2.0	0.001	1	ND<5.0	ND<100	
1885-02-CM-060	Concrete	NA	20.0	20.0	ND<0.5	8.7JM	18	18	-	-	N	-	-	ND<2.0	0.003	1	ND<5.0	ND<100	
1885-02-CM-061	Concrete	NA	20.0	20.0	ND<0.5	9.8JM	20	20	-	N	+-	-	-	ND<2.0	-0.001	1	ND<5.0	ND<100	
1885-02-CM-061MS-NC	Concrete	211	20.0	20.0	NA	NA	NA	NA	N	N	N	+-	-	NA	0.020	1	ND<5.0	ND<100	
1885-02-CM-061MSD-NC	Concrete	211	20.0	20.0	NA	NA	NA	NA	N	N	N	+	+-	NA	0.113	1	NC	229	
1885-02-CM-061MS-NG	Concrete	100	20.0	20.0	NA	NA	NA	NA	N	N	N	+	+	152	O	1	NC	NC	
1885-02-CM-061MSD-NG	Concrete	100	20.0	20.0	NA	NA	NA	NA	N	N	N	+	+	159	O	1	NC	NC	
1885-02-CM-062	Concrete	NA	20.0	20.0	ND<0.5	7.3JM	15	15	-	-	N	-	-	ND<2.0	0.001	1	ND<5.0	ND<100	
1885-02-CM-063	Concrete	NA	20.0	20.0	ND<0.5	11.5JM	24	24	-	-	N	-	-	ND<2.0	0.003	1	ND<5.0	ND<100	
1885-02-CM-064	Concrete	NA	20.0	20.0	ND<0.5	4.2JM	9	9	+-	+-	N	-	-	ND<2.0	0.000	1	ND<5.0	ND<100	
1885-02-CM-065	Concrete	NA	20.0	20.0	ND<0.5	6.9JM	14	14	-	-	N	-	-	ND<2.0	0.003	1	ND<5.0	ND<100	
1885-02-CM-066	Concrete	NA	20.0	20.0	ND<0.5	7.6JM	16	16	-	-	N	-	-	ND<2.0	0.002	1	ND<5.0	ND<100	
1885-02-CM-100	Concrete	NA	20.0	20.0	ND<0.5	3.5JB,J	7	7	+	-	N	-	-	ND<2.0	-0.001	1	ND<5.0	ND<100	
1885-02-CM-100A	Concrete	NA	20.0	20.0	ND<0.5	4.4JB,J	9	9	N	N	N	-	-	ND<2.0	0.000	1	ND<5.0	ND<100	
1885-02-CM-100 Bottom	Concrete	NA	20.0	20.0	NA	NA	NA	NA	N	N	N	-	-	ND<2.0	0.000	1	ND<5.0	ND<100	
1885-02-CM-101	Concrete	NA	20.0	20.0	ND<0.5	2.2JB,J	5	5	-	-	N	-	-	ND<2.0	0.001	1	ND<5.0	ND<100	
1885-02-CM-102	Concrete	NA	20.0	20.0	ND<0.5	3.4JM,J	7	7	-	-	N	-	-	ND<2.0	0.040	1	6.5	81	*Interference- Yellow Color
1885-02-CM-103	Concrete	NA	20.0	20.0	ND<0.5	3.5JM,J	7	7	-	N	+-	-	-	ND<2.0	0.000	1	ND<5.0	ND<100	
1885-01-CM-036-EJM	EJM	NA	5.0	50.0	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND<25	
1890-01B-CM-042-EJM	EJM	NA	5.0	50.0	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	130JC	
1890-01B-CM-046-EJM	EJM	NA	5.0	50.0	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	126JC	
1885-03S-CM-049-EJM	EJM	NA	5.0	50.0	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	92JC	
1885-03-CM-053-EJM	EJM	NA	5.0	50.0	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND<25	
1885-02-CM-064-EJM	EJM	NA	5.0	50.0	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	ND<25	
EQ-RINSE 12/2/05	Water	NA	NA	NA	ND<0.65	0.25J,J	0.57	0.57	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
EQ-RINSE 12/6/06	Water	NA	NA	NA	ND<0.65	0.28J,J	0.63	0.63	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
EQ-RINSE 12/7/06	Water	NA	NA	NA	ND<0.65	0.29J,J	0.65	0.65	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	

(B) = Sample re-analysis by Modified CRREL method
(C) = Sample duplicate re-analysis by Modified CRREL method
Q= Elevated reporting Limit
J = Estimated result. Result is less than reporting limits.
JS = Estimated result. Surrogate recovery is outside stated control limits and reanalysis was outside hold time.
JM = Estimated result. MS/MSD recovery is outside stated control limits.
JB = Estimated result. Method blank contains contamination.
JC = Results are estimates. Values are based on a calibration using NC spiked into blank CM matrix extract.
ND = Not detected at the specified method detection limit
NA = Not analyzed or not applicable
+ = Detected
- = Not detected
+- = Possible detection; slight coloration, but difference from blank color was inconclusive

Table B.2-4 BAAAP/ESTCP Field Demonstration Wood Analysis- QC Sample Summary

			NG GC/TID	Shaw Modified CRREL NG+NC	
Sample Identification	Matrix	QC Sample Spike Description mg/Kg	Conc mg/Kg	Analyzed conc as NG	Analyzed conc as NC
BI-BLK-001-WD-NG	Wood	NA	ND<5.0	ND<5.0	ND<10.0
BI-LCS-001-WD-NG	Wood	100	102	110	NA
BI-LCS-001-WD-NC	Wood	211	NA	NA	231
6657-02I-WD-003	Wood	NA	ND<5.0	ND<5.0	ND<10.0
6657-02I-WD-003A	Wood	NA	ND<5.0	ND<5.0	ND<10.0
6709-17-WD-019	Wood	NA	44.5	83.6	157
6709-17-WD-019MS-NG	Wood	200	217	544	NA
6709-17-WD-019MSD-NG	Wood	200	238	625	NA
6709-17-WD-019MS-NC	Wood	421	NA	NA	770
6709-17-WD-019MSD-NC	Wood	421	NA	NA	779
6709-17-WD-020	Wood	NA	25.4	89.8	165
6709-17-WD-020A	Wood	NA	25.9	120	204
BI-BLK-002-WD-NG	Wood	NA	ND<5.0	ND<5.0	ND<10.0
BI-LCS-002-WD-NG	Wood	50	46.1	44.6	NA
BI-LCS-002-WD-NC	Wood	211	ND<5.0	NA	276
BI-BLK-003-WD-NG	Wood	NA	ND<5.0	ND<5.0	ND<10.0
BI-LCS-003-WD-NG	Wood	200	161	275	389
BI-LCS-003-WD-NC	Wood	211	NA	111	169
1890-01-WD-022	Wood	NA	ND<5.0	ND<5.0	ND<10.0
1890-01-WD-022MS-NG	Wood	100	101	102	NA
1890-01-WD-022MSD-NG	Wood	100	84.8	100	NA
1890-01-WD-022MS-NC	Wood	211	NA	NA	220
1890-01-WD-022MSD-NC	Wood	211	NA	NA	237
1890-01-WD-028	Wood	NA	ND<5.0	21.1	34.8
1890-01-WD-028A	Wood	NA	ND<5.0	22.5	36.7
5024-000-WD-033	Wood	NA	ND<20	1817	2857
5024-000-WD-033A	Wood	NA	ND<20	1782	2811

ND = Not detected at the specified method detrection limit

NA = Not analyzed or not applicable

MS = Matrix Spike MSD= Matrix Spike Duplicate

A = Duplicate Sample, B = Triplicate Sample, C = Quadruplicate Sample

NC = nitrocellulose NG = nitroglycerine

Table B.2-5 BAAAP/ESTCP Field Demonstration Soil Analysis- QC Sample Summary

Sample Identification	Matrix	QC Sample Spike Description mg/Kg	GC/TID NG Conc mg/Kg	CRREL NG+NC Conc as NC mg/kg	Shaw Modified CRREL NG+NC Conc as NC mg/kg
BI-BLK-001-SS-NG	Soil	NA	ND<2.0	ND<25	ND<4
BI-LCS-001-SS-NG	Soil	50	45.6	56.1	54
BI-LCS-001-SS-NC	Soil	200	NA	255	163
1885-02-SS-071	Soil	NA	ND<2.0	ND<25	ND<5
1885-02-SS-071MS NG	Soil	37.5	39.1	40.9	67
1885-02-SS-071MSD NG	Soil	37.5	39.5	36.1	75
1885-02-SS-071MS NC	Soil	37.5	NA	ND<25	ND<38
1885-02-SS-071MSD NC	Soil	37.5	NA	ND<25	ND<38
1885-02-SS-072	Soil	NA	22.0	4290	7570
1885-02-SS-072A	Soil	NA	44.5	7500	8610
1890-01B-SS-081	Soil	NA	ND<2.0	ND<25	42
1890-01B-SS-081A	Soil	NA	ND<2.0	ND<25	ND<6
1890-01B-SS-081B	Soil	NA	NA	NA	ND<5
1890-01B-SS-081C	Soil	NA	NA	NA	ND<5
BI-BLK-002-SS-NC/NG	Soil	NA	ND<2.0	ND<25	ND<2
BI-LCS-002-SS-NG	Soil	50	55.0	50.8	78
BI-LCS-002-SS-NC	Soil	200	NA	169	NS
1885-02-SS-083	Soil	NA	ND<2.0	44.8	163
1885-02-SS-083A	Soil	NA	ND<2.0	ND<25	183
1885-02-SS-087	Soil	NA	ND<2.0	53.3	251
1885-02-SS-087MS NG	Soil	50	55.5	33.1	184
1885-02-SS-087MSD NG	Soil	50	54.8	34.3	578
1885-02-SS-087MS NC	Soil	316	NA	63.8	281
1885-02-SS-087MSD NC	Soil	316	NA	85.7	195
1885-02-SS-093	Soil	NA	ND<2.0	ND<25	ND<45
1885-02-SS-093A	Soil	NA	ND<2.0	ND<25	ND<15

ND = Not detected at the specified method detrection limit
NA = Not analyzed or not applicable
MS = Matrix Spike
MSD= Matrix Spike Duplicate
A = Duplicate Sample, B = Triplicate Sample, C = Quadruplicate Sample
NC = nitrocellulose NG = nitroglycerine

Table B.2-6 BAAAP/ESTCP Field Demonstration Concrete Analysis- QC Sample Summary

Sample	Matri	QC Sample Description	N GC/TI	NG+NC	
			Conc mg/Kg	Analyzed as NG	Analyzed conc as NC
BI-BLK-001-CM-NG	Concret	N	ND<2.0	ND<5.0	ND<100
BI-LCS-001-CM-NG	Concret	50	41	53.7	NC
BI-BLK-001-CM-NC	Concret	N	N	ND<5.0	ND<100
BI-LCS-001-CM-NC	Concret	211	N	ND<5.0	ND<100
9590-000-CM-034	Concret	N	ND<2.0	ND<5.0	ND<100
9590-000-CM-034A	Concret	N	ND<2.0	ND<5.0	ND<100
1885-01-CM-035	Concret	N	ND<2.0	ND<5.0	ND<100
1885-01-CM-035B	Concret	N	ND<2.0	ND<5.0	ND<100
1890-01B-CM-038	Concret	N	ND<2.0	ND<5.0	ND<100
1890-01B-CM-038MS-NC	Concret	211	ND<2.0	NC	ND<100
1890-01B-CM-038MSD-NC	Concret	211	ND<2.0	NC	114
1890-01B-CM-038MS-NG	Concret	100	172	OR	NC
1890-01B-CM-038MSD-NG	Concret	100	156	OR	NC
1890-01B-CM-043	Concret	N	ND<2.0	ND<5.0	ND<100
1890-01B-CM-043A	Concret	N	ND<2.0	ND<5.0	ND<100
1890-01B-CM-046	Concret	N	2.52	8.8	124
1890-01B-CM-046A	Concret	N	1.44	9.0	128
BI-BLK-002-CM-NG	Concret	N	ND<2.0	ND<5.0	ND<100
BI-LCS-002-CM-NG	Concret	50	48.2	45.2	NC
BI-BLK-002-CM-NC	Concret	N	N	ND<5.0	ND<100
BI-LCS-002-CM-NC	Concret	211	N	ND<5.0	ND<100
1885-02-CM-061	Concret	N	ND<2.0	ND<5.0	ND<100
1885-02-CM-061MS-NC	Concret	211	N	ND<5.0	ND<100
1885-02-CM-061MSD-NC	Concret	211	N	NC	229
1885-02-CM-061MS-NG	Concret	100	152	NC	NC
1885-02-CM-061MSD-NG	Concret	100	159	NC	NC
1885-02-CM-100	Concret	N	ND<2.0	ND<5.0	ND<100
1885-02-CM-100A	Concret	N	ND<2.0	ND<5.0	ND<100

ND = Not detected at the specified method detection limit

NA = Not analyzed or not applicable

MS = Matrix Spike

MSD= Matrix Spike

A = Duplicate Sample, B = Triplicate Sample, C = Quadruplicate Sample

NC = nitrocellulose NG = nitroglycerine

Appendix B.3
STL Data Validation Reports

Data Validation Summary Report
ESTCP Demonstration Plan
Wisconsin

1.0 Introduction

Level III data validation was performed on 100 percent of the environmental samples collected for the December 2005 sampling event. The analytical data consisted of sample delivery groups (SDG's) G5L090406, G5L090407, G5L130251, G5L130268, G5L130276, G5L130291, and G5L280254, which were analyzed by STL. The chemical parameters for which the samples were analyzed and validated are identified below:

Parameter (Method)
Nitroglycerin by SW846 8332
Nitrocellulose by MCAWW 353.2

2.0 Procedures

The sample data were validated following the logic identified in the 1999 *EPA Contract Laboratory Program National Functional Guidelines for Organic Review* for all areas. Specific quality control (QC) criteria as identified in analytical methods, and laboratory standard operating procedures (SOP) were applied to all sample results. In light of applying CLP guidelines to SW846 methods and evaluating the usability of the data during the validation process, specific QC criteria were determined to address all target compounds and are identified in this report for each parameter, as well as in the validation checklists, which function as worksheets. All completed validation checklists are included in Attachment A. For those analytical methods not addressed by the CLP guidelines, the validation was based on the method requirements (i.e., SW846, Code of Federal Regulations, SOPs) and technical judgement, following the logic of the CLP validation guidelines.

3.0 Summary of Data Validation Findings

The overall quality of the data was determined to be acceptable with minimal qualification. The only rejected data ("R" qualified) were samples that were reanalyzed and have more than one set of results reported. The "R" qualifier was assigned to the samples with more than one set of results to indicate that a given result should not be used to characterize a particular constituent or an analysis for a given sample.

Individual validation reports have been prepared for each parameter, and the overall results of the validation findings are summarized in this report. A listing of the validation qualifiers and the reason codes, along with their definitions, can be found in Attachment A. The following section highlights the key findings of the data validation for each analysis.

4.0 Analysis-Specific Data Validation Summaries

4.1 Nitroglycerine by HPLC SW846 8332

Overall, the data are of good quality and are usable as reported by the laboratory with the exceptions noted below. Data were reviewed for the following:

Holding Times

Technical holding time criteria were met for all samples with the following exception(s):

SDG	Samples Affected	Compound(s)	Validation Qualifier
G5L130251	*1885-02-SS-072, -072A	Nitroglycerine	J
G5L280254	*1885-02-SS-083	Nitroglycerine	J

*Note that the highest results were chosen for reporting between samples with low surrogates and re-analysis (due to low surrogate recoveries) outside of hold time.

Initial and Continuing Calibration

The initial calibration (ICAL) and continuing calibrations (CCAL) associated with the project samples met QC criteria.

Blanks

The 5X rule for contaminants found in the associated method and equipment rinse blanks were applied to all sample results. All were found to be acceptable.

SURROGATE RECOVERIES

Surrogate recovery QC criteria were met with the following exception(s):

SDG	Samples Affected	Compound(s)	Validation Qualifier
G5L130251	*1885-02-SS-069, -080	Nitroglycerine	J
G5L280254	*1885-02-SS-083A, -084, -099, -072A	Nitroglycerine	J/UJ

*Note that the highest results were chosen for reporting between samples with low surrogates and re-analysis (due to low surrogate recoveries) outside of hold time.

Note for SDG G5L090407 non-detect sample 5024-000-WD-011 had low surrogate recoveries but was diluted (1-5), and non-detect sample 1890-01-WD-022 had high surrogate recoveries. No qualifiers were applied.

Matrix Spike / Matrix Spike Duplicate

Matrix Spike/Matrix Spike Duplicate (MS/MSD) analysis was performed for the project

samples, and all QC criteria were met with the following exception(s):

SDG	Samples Affected	Compound(s)	Validation Qualifier
G5L130251	*1885-02-SS-072	Nitroglycerine	J
G5L280254	*1885-02-SS-083	Nitroglycerine	J

***Original batch (includes all SDG samples) MS/MSDs were within QC limits. Re-extracted samples (outside of hold time) used for reporting were also used as MS/MSDs; therefore, only the re-analyzed samples were qualified due to MS/MSD %recovery.**

Note that MS/MSD %recoveries were not calculated for SDG G5L090407 because the original sample was diluted beyond the ability to quantitate a recovery.

Laboratory Control Sample

Laboratory Control Sample (LCS) analysis was performed for the project samples, and all QC criteria were met.

Field Duplicates

Original and field duplicate results were evaluated and no problems were identified.

2nd Column Confirmation
Percent difference between columns was within QC limits with the following exception(s):

SDG Number	Samples Affected	Compound(s)	Validation Qualifier
G5L130251	1885-02-SS-072A	Nitroglycerine	J

Note SDG G5L0130251 original sample 1885-02-SS-072 results with %D between columns above the QC limits was rejected in favor of higher re-analysis results outside of hold time.

Quantitation
Results quantitated between the method detection limit (MDL) and the reporting limit (RL), which the lab qualified as "J", were qualified as estimated "J" unless blank contamination was present or the results were rejected. Results rejected in favor of a preferred result (e.g., due to dilution or reanalysis) were qualified as rejected "R."

4.2 Nitrocellulose MCAWW 353.2

Overall, the data are of good quality and are usable as reported by the laboratory with the exceptions noted below. Data were reviewed for the following:

Holding Times

Technical holding time criteria were met for all samples.

Initial and Continuing Calibration

The initial calibration (ICAL) and continuing calibrations (CCAL) associated with the project

samples met QC criteria.

Blanks

The 5X rule for contaminants found in the associated method blanks and equipment rinse was applied to all sample results. All were found to be acceptable with the following exception(s):

SDG Number	Samples Affected	Compound(s)	Blank Contaminate	Validation Qualifier
G5L090406	1890-01-WD-023, -024, -026, -027, -028, -028A, -030, -031	Nitrocellulose	Method	U
G5L130268	1885-03S-CM-047	Nitrocellulose	Method	U
G5L130291	1885-02-CM-100, -101, -102, -103, -100A	Nitrocellulose	Method	*UJ
G5L280254	**1885-02-SS-088, -090, -094, -096	Nitrocellulose	Method	U

*** Results were "UJ" qualified due to low MS/MDS % recoveries.**
****Original sample results less than 10X the method blank contamination were re-analyzed to confirm their results. Original results were chosen over re-analysis and blank qualified ("U").**

Matrix Spike / Matrix Spike Duplicate

Matrix Spike/Matrix Spike Duplicate (MS/MSD) analysis was performed for the project samples, and all QC criteria were met with the following exception(s):

SDG Number	Samples Affected	Compound(s)	Validation Qualifier
G5L090407	6709-17-WD-012, -013, -014, -015, -016, -017, -018, -019, -020, -020A, -021, -022	Nitrocellulose	J
G5L130276	1885-03S-CM-048, -48, -050 1885-03-CM-051, -052 -053, -054, -055, -056 1885-02-CM-057, -058, -059, -060, -061, -062, -063, -064, -065, -066	Nitrocellulose	J
G5L130291	1885-02-CM-100, -100A, -101, -102, -103 9590-000-CM-034A 1890-01B-CM-043A, -046A 1885-02-CM-100A	Nitrocellulose	J/UJ*

*** Results were "UJ" qualified due to method blank contamination.**

Note that MS/MSD %recoveries were not calculated because sample amounts were greater than 4X spike amounts for SDG's G5L130251 and G5L130268.

Laboratory Control Sample

Laboratory Control Sample (LCS) analysis was performed for the project samples, and all QC criteria were met.

Field Duplicates

Original and field duplicate results were evaluated and no problems were identified with the following exception(s):

SDG Number	Samples Affected	Compound(s)	Validation Qualifier
G5L130251	1885-02-SS-081 (original), 1885-02-SS-081A (FD),	Nitrocellulose	J

Quantitation

No results were reported below the reporting limit (RL). Results rejected in favor of a preferred result (e.g., due to dilution or reanalysis) were qualified as rejected "R."

Attachment A

Data Validation Qualifier Entry Verification Report

Validation Qualifiers

U Not detected. The compound/analyte was analyzed for, but not detected above the associated reporting limit.

J The compound/analyte was positively identified; the reported value is the estimated concentration of the constituent detected in the sample analyzed.

UB The concentration reported was detected significantly above the levels reported in the associated equipment rinse samples and/or laboratory method and trip blanks. (5X/10X Rule was applied).

R/UR The reported sample results are rejected due to the following:

1. Severe deficiencies in the supporting quality control data.

2. Anomalies noted in the sampling and/or analysis process which could affect the validity of the reported data.

3. The presence or absence of the constituent cannot be verified based on the data provided.

4. To indicate not to use a particular result in the event of a reanalysis.

UJ The compound/analyte was analyzed for, but not detected above the established reporting limit. However, review and evaluation of supporting QC data and/or sampling and analysis process have indicated that the “nondetect” may be inaccurate or imprecise. The nondetect result should be estimated.

Validation Reason Code Definitions

Reason Code	Definition
01	Sample received outside of 4+/-2 degrees Celsius
01A	Improper sample preservation
02	Holding time exceeded
02A	Extraction
02B	Analysis
03	Instrument performance – outside criteria
03A	BFB
03B	DFTPP
03C	DDT and/or Endrin % breakdown exceeds criteria
03D	Retention time windows
03E	Resolution
04	Initial calibration results outside specified criteria
04A	Compound mean RRF QC criteria not met
04B	Individual % RSD criteria not met
04C	Correlation coefficient >0.995
05	Continuing calibration results outside specified criteria
05A	Compound mean RRF QC criteria not met
05B	Compound % D QC criteria not met
06	Result qualified as a result of the 5x/10x blank correction
06A	Method or preparation blank
06B	ICB or CCB
06C	ER
06D	TB
06E	FB
07	Surrogate recoveries outside control limits
07A	Sample
07B	Associated method blank or LCS
08	MS/MSD/Duplicate results outside criteria
08A	MS and/or MSD recovery not within control limits (accuracy)
08B	% RPD outside acceptance criteria (precision)
09	Post digestion spike outside criteria (GFAA)
10	Internal standards outside specified control limits
10A	Recovery
10B	Retention time
11	Laboratory control sample recoveries outside specified limits
11A	Recovery
11B	% RPD (if run in duplicate)
12	Interference check standard
13	Serial dilution
14	Tentatively identified compounds
15	Quantitation
16	Multiple results available; alternate analysis preferred
17	Field duplicate RPD criteria is exceeded
18	Percent difference between original and second column exceeds QC criteria
19	Professional judgement was used to qualify the data
20	Pesticide clean-up checks
21	Target compound identification
22	Radiological calibration
23	Radiological quantitation
24	Reported result and/or lab qualifier revised to reflect validation findings

ESTCP Program Office

901 North Stuart Street
Suite 303
Arlington, Virginia 22203

(703) 696-2117 (Phone)
(703) 696-2114 (Fax)

e-mail: estcp@estcp.org
www.estcp.org